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CHEMICAL KINETICS OF ENTRY INTO THE MARTIAN ATMOSPHERE

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UNITED STATES AIR FORCE
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ABSTRACT

The reactions between carbon monoxide and oxygen to form carbon dioxide have been examined in two separate experimental studies. In the first study a mixture of carbon monoxide and oxygen was introduced into a shock tube. The mixture then was heated by a shock wave and the rate of formation of carbon dioxide was determined. The carbon dioxide concentration was followed by observing the intensity of the infrared radiation at 4.25μ emitted by the heated carbon dioxide. Rate constants were obtained. However, it was shown that if the amount of water vapor in the system was greater than 7 ppm, the primary reactions were governed by the hydrogen-oxygen system of reactions. Hence, it was impossible to obtain reliable rate constants for the CO-O_2 system of reactions. The elimination of such minute quantities of moisture is virtually impossible.

The second experimental study involved expanding a high temperature mixture of CO_2, CO and O_2 through a supersonic expansion nozzle. From a measurement of the pressure profile down the nozzle the chemical state of the gas can be determined. Extensive computer programs were formulated for this phase of the investigation. Unfortunately the contract period came to an end at the conclusion of the calibration experiments. Hence, no information was obtained concerning the recombination of carbon dioxide.

FOREWORD

This final report was prepared by E. Stokes Fishburne, K. R. Bilwakesh and R. Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University, on Contract No. AF 33(657)-8951, Project 7065, Aerospace Simulation Techniques Research. The research on this task was administered under the direction of the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force, with Mr. John Goresh, Fluid Dynamics Facilities Laboratory, as Contract Monitor.

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SECTION I

INTRODUCTION

The study of entry into planetary atmospheres, including earth, requires a detailed knowledge of both the atmospheric structure and the chemical composition. This information is necessary in order that heating rates and lift and drag may be computed. Of all the planetary atmospheres, entry into the earth's atmosphere has received the most attention for obvious reasons. Studies involving reentry into the earth's atmosphere have been conducted in low temperature wind tunnels, high temperature wind tunnels, shock tubes, and shock tunnels. The information which has been obtained include reaction rate constants, convection heating, radiation heating, microwave attenuation, etc. On the other hand very little information is available on the composition of the other planetary atmospheres much less on the other aspects of planetary entry.

The subject of most immediate interest is Mars. The recent Mariner trip revealed much concerning the surface of Mars but somewhat less on the atmosphere. At the present time several estimates of the Martian atmosphere are available. The general consensus is that the surface pressure is low and that the atmosphere contains a large amount of carbon dioxide. The best estimates of the carbon dioxide content is that obtained by astronomers in the study of the infrared spectra of Mars. The low surface pressure and the generally high entry velocity pose a very definite problem in obtaining a soft landing on Mars. Many of these aspects of the Martian atmosphere will be discussed in considerably more detail in the following section.

The wind tunnel simulation of entry into the Martian atmosphere requires that carbon dioxide be heated to rather high temperatures, above 4000°K. As the gas expands through the nozzle the gas may or may not be in chemical equilibrium. For an accurate assessment of the gas at the nozzle exit and for the determination of the free stream temperature and composition we must have a knowledge of the chemical reaction rates involved in the process. At the present time some of these rates are known quite well while others are not known within a factor of 10 to 100. One of the purposes of this study was to determine, by expanding heated carbon dioxide through a nozzle, the approximate values of the rate constants involved.

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SECTION II

THE MARTIAN ATMOSPHERE

In the last few years several models have been proposed for the Martian atmosphere. Values of the surface temperature have ranged from 200°K to 300°K (Ref. 1). Estimates of the surface pressure have ranged from 10 mb (Ref. 2) to 133 mb (Ref. 1). Estimates of the chemical composition have been as different as the estimates of the surface pressure. The amount of CO_2 has been estimated to be anywhere between 0.7% and 100%, depending on the surface pressure (Ref. 3). The remainder of the atmosphere is either nitrogen, argon, or both. All of the estimates of the carbon dioxide concentration are based primarily on spectrographic observation of the carbon dioxide absorption bands (Ref. 4). The observed absorption is caused by the passage of solar radiation through the Martian atmosphere to the surface, reflecting from the surface, and passing through the atmosphere again. Thus the indicated absorption is an integrated effect of the total carbon dioxide in the atmosphere. Recent spectrographic observations of Mars by Owen (Ref. 5) and Spinrad et al. (Ref. 6) indicate that, if the atmosphere is assumed to be pure carbon dioxide, the surface pressure should be 5-7 mb. Assuming that the atmosphere may contain nitrogen the surface pressure may be as high as 20 mb but no higher. These values were determined by studying the pressure broadening of the spectral lines. Recent measurements by Mariner IV (Ref. 7) indicate a surface pressure of 5-6 mb. The measurements made by Mariner IV did not depend to any large extent on the chemical composition of the atmosphere. Assuming a 100% CO_2 atmosphere the surface pressure was found to be between 4.1 and 5.7 mb. Assuming 20% argon or nitrogen and 80% CO_2 the surface pressure becomes between 5.0 and 7.0 mb. From the Mariner IV data and the spectroscopic observations of Ref. 5 and 6, we find that a reasonable estimate of the surface pressure is 6.0 ± 1 mb and that the atmosphere is composed almost entirely of carbon dioxide with, at most, about 20% argon or nitrogen. Furthermore, these pressures and mixtures indicate a surface temperature of about 180°K ± 25°K. Such an atmosphere would explain both the spectrographic observations as well as the Mariner observations. Although the surface temperature is estimated to be about 180°K, seasonal and diurnal variations could easily produce a temperature of 275-300°K at the equator.

The next question concerns the amount of moisutre in the atmosphere of Mars. No permanent bodies of water could exist on Mars since the surface conditions are below the triple point of water. In the past, it has been assumed that the polar caps of Mars were composed of ice or a type of H_2O permafrost. Recent calculations by Leighton and Murray (Ref. 8) strongly indicate that the polar caps may be frozen CO_2 or CO_2 permafrost. These calculations were based on the heat balance of Mars and the known vapor pressure curve of carbon dioxide. They also indicate a relatively low amount of moisture in the atmosphere. It is estimated that surface pressure of moisture is of the order of 1 micron of

Hg. This small amount is of considerable importance in the reaction kinetics of carbon monoxide and oxygen.

No reliable information exists on the existence of other gases, other than atomic oxygen and carbon monoxide, in the Martian atmosphere. Kiess, et al. (Ref. 9) have reported the detection of the oxides of nitrogen but these are unconfirmed. Several different atmospheric structures are given in the literature (Refs. 10, 11). Basically, the temperature and pressure profiles are in fair agreement but the extent of the E, F_1 and F_2 layers are somewhat unknown. A typical structure is that given by Donahue (Ref. 12) and indicated in Table I. Donahue assumed a surface temperature of 220°K and a surface pressure of 7 mb. The concentrations of CO_2, CO and O are given in molecules/cc.

TABLE I - SAMPLE ATMOSPHERIC STRUCTURE OF MARS

Alt. (km)	T (°K)	CO_2	O	CO
0	220	2×10^{17}		
50	160	1×10^{15}		
100	160	2×10^{12}	3×10^{10}	3×10^{10}
150	180	4.6×10^{9}	2×10^{9}	6×10^{8}
200	320	2.5×10^{7}	2×10^{8}	2.2×10^{7}
250	400	2.4×10^{5}	7×10^{7}	1.6×10^{6}

From Table I it is apparent that the amount of CO_2 decreases with increasing altitude and at an altitude of about 100 km the CO_2 begins to dissociate into CO and O due to photoionization and other processes. The molecular densities are considerably lower than those found in the atmosphere of earth. The addition of nitrogen or argon would not appreciably affect this profile.

In summary, we find that the best estimates of the Martian atmosphere indicate that the carbon dioxide content is at least 80%, probably higher, with the remainder being either nitrogen, or argon, or both. The best estimates of the surface temperature and pressure are 180°K and 6 mb. Furthermore, it is doubtful if the partial pressure of moisture close to the surface is much greater than 1 micron of Hg.

SECTION III

ENTRY CONDITIONS

Because of the atmosphere, or lack of an atmosphere, as we know it, on Mars, the entry conditions are somewhat different than those encountered in entering the earth's atmosphere. The maximum heating of a ballistic body on entering the earth's atmosphere occurs at a pressure of about 6 mb which corresponds to an altitude of about 110,000 feet. Maximum heat transfer on entering the Martian atmosphere should occur at about the same pressure (Ref. 13). Hence, we would expect that maximum heat transfer depends, to a very large extent, on the entry velocity and the chemical composition. The entry velocities will be between 19,000 feet per second and 36,000 feet per second (Ref. 14) with a theoretical minimum of 16,000 feet per second. Gruszczynski and Thomas (Ref. 15) have shown that at flight velocities below 25,000 feet per second the primary radiation is that due to the molecular species CN and CO. In fact, CN is a very important radiating species. Above 25,000 feet per second the radiation is due primarily to atomic lines.

The main uncertainty in the heating problem lies in the formation of CN and the actual amount of CN in the equilibrium gas mixture. Theoretical computations of the CN concentration in an equilibrium mixture depend on the value of the equilibrium constant which, in turn, depends on the dissociation energy of CN. Values of the dissociation energy range from 7.5 ev to 8.2 ev (Ref. 16). Such a discrepancy can affect the concentration of CN by a factor of about 3. Of course, if the atmosphere of Mars does not contain any nitrogen then CN would not be formed by the high temperature. However, CN may be formed depending on the type of ablating material which is used.

Another aspect of entry into the Martian atmosphere concerns the wind tunnel simulation of the entry conditions. Conventional wind tunnels have an upper temperature limitation of about 2000°K. At these temperatures CO_2 does not dissociate appreciably. Hence, the expansion process only involves the unreacted gas mixture. In this case the only problem of any importance is the solidification of the carbon dioxide as it expands to low temperatures. The computation of wind tunnel conditions leading to solidification is fairly straightforward. With chemical reactions the computation of the flow properties is not very easy. Figure 1 indicates the variation of pressure with area ratio for equilibrium flow and for frozen flow. The frozen flow computation is based on a sudden freezing of the chemical species at a Mach number of 1.771. Figures 2 and 3 indicate the temperature and velocity, respectively, as a function of area ratio. It is quite clear from these figures that there is a wide difference between the equilibrium and frozen properties of the gas flow. To compute the actual variations in the gas properties as a function of area ratio in a given nozzle accurate values must be known for the rate constants of the various chemical reactions involved.

Zonars (Ref. 17) has developed a computer program which computes the gasdynamic properties of the gas if the appropriate rate constants are known. Herein lies one of the basic problems involving the chemistry of the Martian atmosphere.

The rate constants of reactions involving the chemical species found in high temperature air are known quite well (Ref. 18). However, only recently have studies been made of the chemical reactions involved in entry into the Martian atmosphere. Practically all of these studies involve the rate of dissociation of carbon dioxide (Ref. 19-23). In general, very little information exists concerning the pertinent chemical reactions. Most information concerning heat transfer in Martian entry is based on equilibium flow behind the shock wave. It is very easy to visualize situations in which equilibrium may not prevail either behind the shock wave or back along the body. For these studies and for an accurate analysis of the state of the gas in a high temperature wind tunnel it is absolutely necessary to have accurate values of the rate constants of the chemical reactions involved.

SECTION IV

PERTINENT CHEMICAL REACTIONS

For an analysis of the possible chemical reactions involved we shall consider separately the pure carbon dioxide atmosphere and the atmosphere containing both carbon dioxide and nitrogen. We shall find also that it is necessary to consider several reactions involving moisture, H_2O, since moisture considerably affects the reaction between oxygen and carbon monoxide.

For the pure carbon dioxide atmosphere we have the following reactions

$$CO_2 + M \longrightarrow CO + O + M \qquad (1)$$

$$CO_2 + O \longrightarrow CO + O + O \qquad (2)$$

$$CO + M \longrightarrow C + O + M \qquad (3)$$

$$CO + O_2 \longrightarrow CO_2 + O \qquad (4)$$

$$CO + O \longrightarrow CO_2 \qquad (5)$$

$$O + O + M \longrightarrow O_2 + M \qquad (6)$$

where M is some third body. Several rates are available for reaction 1 (Ref. 19-23). The rate constant obtained by these individuals are shown in Figure 4 for an argon diluent. It has been shown that the rate of decomposition of CO_2 is bimolecular. The best rate constant which fits all of the data over the temperature range 3000°K - 11,000°K is indicated by the dashed line and represented by the rate constant

$$k_1 = 2.5 \times 10^{11} T^{1/2} \exp(-76{,}500/RT)$$

Rate constants which were obtained for the dissociation of carbon dioxide in an excess of nitrogen are given in Ref, 20 and 22.

The rate constant for reaction 2 has not been determined, although Fishburne, Bilwakesh, and Edse (Ref. 22) have observed a slight increase in the rate of disappearance of CO_2 in a shock-heated mixture containing argon and carbon dioxide.

The dissociation of carbon monoxide has been estimated by Bortner (Ref. 24) to be

$$k_3 = 6 \times 10^{15} \exp(-250{,}000/RT)$$

Reaction 4 has been studied by Sulzmann et al. (Ref. 25) in a gaseous system containing carbon monoxide, oxygen, and argon. From a measurement of the induction time, the time before the mixture "exploded," they were able to deduce a rate constant for this reaction

$$k_4 = (3.5 \pm 1.6) \times 10^{12} \exp\left(\frac{-51000 \pm 7000}{RT}\right)$$

However, it was felt that this value was somewhat uncertain because of the hydrogenous material in the gas mixture from the commercial gases.

Reaction 5 has been studied by Mahan and Solo (Ref. 26) and Avramenko and Kolesnikova (Ref. 27) and the rate constants were found to be

$$k_5^A = 1.8 \times 10^9 T^{1/2} \exp(-3000/RT)$$

and

$$k_5^M = 10^{10} \exp(-4000/RT)$$

where the A superscript indicates Avramenko and the M, Mahan. The numerical values of the rate constants differ by about a factor of 10 in the temperature range in which the reaction was studied, 300-600°K.

The peculiar problem in the formation of CO_2 from CO and O is that one would inherently predict that the reaction would require a third body, as in reaction 6, to remove some of the energy, otherwise the molecule would redissociate. However, both of the investigations presented in Refs. 26 and 27 strongly indicate that the reaction is bimolecular (two-body) rather than trimolecular (three-body). There are many aspects of this reaction which are too involved for the discussion here. However, it should be pointed out that a three-body recombination has not been observed, which means that the primary mechanism for the generation of CO_2 from CO and O is reaction 5 and not the reverse of reaction 1.

The reverse of reaction 6 has been investigated by many individuals, a list of which has been presented in Ref. 18. The reaction rate constant is given by

$$M = A, N, NO \; ; \qquad k_{-6,A} = 2.5 \times 10^{11} T^{1/2} (D/RT)^{1.5} \exp(-D/RT)$$

$$M = N_2 \qquad k_{-6,N_2} = 2k_{-6,A}$$

$$M = O_2 \qquad k_{-6,O_2} = 9k_{-6,A}$$

$$M = O \qquad k_{-6,O} = 25k_{-6,A}$$

where D = 118,000 cal/mole which is the dissociation energy of molecular oxygen.

Normally the reverse of the reactions indicated above, reactions 1-6, are calculated from the known forward reaction rate constant, k_f, and the equilibrium constant K_{eq}. Hence

$$k_r = k_f/K_{eq}$$

Values of K_{eq} can be obtained from Ref. 16. As indicated above it has been determined that the reverse of reaction 1 cannot be obtained by this relation. Since the rate of reaction 2 is not known we cannot obtain a value for the reverse reaction. At the present time there is no

reason to expect that the reverse of reaction 3 could not be given by the above relation. From the data available it would be unwise to assume that the reverse of reaction 4 could be obtained through the equilibrium constant. The difficulty with reaction 5 is the choice of the equilibrium constant. It is quite obvious that the CO_2 molecule represented in this reaction is not in its ground electronic state. Hence, any value of the equilibrium constant would be only an estimate. Kieffer and Lutz (Ref. 28) have shown that the rate constant of reaction 6 can be represented quite satisfactorily by the relation involving the equilibrium constant.

From the brief summary presented above of reactions likely to occur in a pure CO_2 atmosphere we find that information on the appropriate rate constants are meager and in some cases unreliable. We have not considered reactions involving C_2 since this would only complicate matters beyond their present state of confusion. Likewise, we have not included any ionization phenomena which should be included in any detailed analysis of the kinetics of a CO_2 atmosphere.

The introduction of the possibility of N_2 in the atmosphere forces us to consider all of the reactions occurring in air, of which Wray (Ref. 18) has a fairly complete list, as well as the formation of CN. The importance of CN has been emphasized previously. The basic questions at this time are how, and at what rate, it is generated. Several possibilities exist for the generation of CN

$$CO + N_2 \longrightarrow CN + NO$$

$$M + C + N \longrightarrow CN + M$$

$$CO + N \longrightarrow CN + O$$

At this time no information is available concerning the rate of formation of CN from any of these reactions.

The presence of moisture in the Martian atmosphere considerably complicates the reaction kinetics of carbon monoxide-oxygen systems. Brokaw (Ref. 29) has shown that the following reactions should be considered in addition to reactions 1-6

$$O + H_2O \longrightarrow OH + OH \qquad (10)$$

$$O + H_2 \longrightarrow OH + H \qquad (11)$$

$$CO + OH \longrightarrow CO_2 + H \qquad (12)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (13)$$

$$H + O_2 \longrightarrow OH + O \qquad (14)$$

Rate constants for these reactions may be obtained from Kaskan and Browne (Ref. 30). Employing these relations Brokaw was able to explain the results obtained by Sulzmann et al. (Ref. 25) if as little as 7 ppm of H_2O were present in the system. Since H_2O is known to exist on Mars in a considerably higher ratio than 7 ppm, it is expected that the resulting chemical kinetics may be affected. Of course it is impossible to determine the exact amount of water vapor in the Martian atmosphere; therefore, this phase of the investigation will remain unknown.

In view of the unknown aspects of many of the reactions it was decided to a) investigate the reactions between CO and O_2 in a shock tube in order to determine the rate constants for reactions 4 and 5, and, b) to shock heat gaseous mixtures containing carbon dioxide and expand the resulting mixture through a nozzle. It was anticipated that a measurement of the axial pressure distribution would provide information from which the rate constant and molecularity of reaction 5 could be determined.

SECTION V

STUDY 1 - THE KINETICS OF THE CARBON MONOXIDE-OXYGEN SYSTEM

The shock tube consisted of a 13-foot-long driver section and a 23-foot-long driver section, both with a 2-inch inner diameter. The shock tube was especially designed for investigation at very low pressures. A six-inch oil diffusion pump was employed to evacuate the driven section of the tube. The leak and/or outgassing rate was less than 0.1 μ/min at all times. Less than one minute after the driven section was filled, the shock wave was generated. The driver section also was evacuated before the driver gas was introduced. Helium was used exclusively as the driver gas. Hydrogen was not employed as the driver gas in order to avoid contamination of the tube wall with hydrogen.

Velocity measurements were made by measuring the time of passage of the shock wave between platinum strips placed 0.5 meter apart. The uncertainty in the velocity measurements was less than 0.3%. The attenuation of the shock wave was found to be negligible.

The temperature behind the shock wave was calculated on the basis of complete thermodynamic equilibrium. At the temperatures employed in this study the vibrational relaxations of O_2 and CO were very rapid and

of no concern. A computer program was formulated to account for the change in the thermodynamic properties of the gas at some distance behind the shock front due to the exothermicity of the carbon dioxide formation.

The progress of the reaction was observed by monitoring the infrared radiation at 4.25 μ. Care was taken to ensure that radiation from carbon monoxide did not invalidate the results. The infrared detection system has been described previously (Ref. 22). A typical oscilloscope trace of the time variation of the intensity of the infrared radiation is shown in Figure 5.

The carbon monoxide and oxygen were premixed in a 12-liter flask which had been evacuated with an oil diffusion pump. Research grade carbon monoxide and oxygen were used in the study. The gases were analyzed and found to contain no detectable trace of hydrogen or moisture (less than 1 ppm). The gases were allowed to remain in the flask for a reasonable length of time to ensure mixing. In several experiments the shock tube was flushed with the test gas and evacuated again before the experiment was conducted. It was found that flushing had no effect on the results.

SECTION VI

THEORETICAL CONSIDERATIONS

When carbon monoxide reacts with oxygen the following reactions may occur

$$CO + O_2 \longrightarrow CO_2 + O \qquad (15)$$

$$CO + O \longrightarrow CO_2^{**} \qquad (16)$$

$$CO + O + M \longrightarrow CO_2^{**} + M \qquad (17)$$

$$CO_2^{**} + O_2 \longrightarrow CO_2 + O + O \qquad (18)$$

$$CO_2^{**} \longrightarrow CO_2^{*} \qquad (19)$$

$$CO_2^{**} + O_2 \longrightarrow CO_2 + O_2 \qquad (20)$$

$$CO_2^{*} \longrightarrow CO_2 + h\nu \qquad (21)$$

$$CO_2^{*} + O_2 \longrightarrow CO_2 + O + O \qquad (22)$$

$$O_2 + O_2 \longrightarrow O_2 + O + O \qquad (23)$$

$$O_2 + O + O_2 \longrightarrow O_3 + O_2 \qquad (24)$$

$$O_3 + O \longrightarrow O_2 + O_2 \qquad (25)$$

$$O_3 + CO \longrightarrow CO_2 + O_2 \qquad (26)$$

The activated molecules, CO_2^* and CO_2^{**}, correspond to excited electronic states of CO_2 as shown in Figure 6. The electronic state given by CO_2^{**} is metastable, since transition to the ground state is optically forbidden due to a spin reversal (Ref. 31). Reaction 19 indicates a radiationless transition between the two electronic states.

In their study, Sulzmann et al. (Ref. 25) assumed that only reactions 15, 16, and 18 were important. On the basis of this assumption and employing Mahan and Solo's rate constant for reaction 16 they obtained for reaction 18 the expression

$$k_{18} = (1.4 \pm 1.1) \times 10^{14} \exp\left(\frac{-39000 \pm 7000}{RT}\right)$$

No rate constant is available for reaction 19 although Clyne and Thrush (Ref. 31) assume that the transition occurs freely. No rate constants are available for reactions 20, 22 and 26. For our study the generation of atomic oxygen by reactions 18 and 22 can be grouped under reaction 18. Clyne and Thrush (Ref. 31) have indicated that the radiative lifetime of the excited state, CO_2^*, is about 50 μ sec. Rate constants are available in the literature for reactions 23 (Ref. 32-34), 24 (Ref. 35, 36) and 25 (Ref. 37, 38).

SECTION VII

ANALYSIS of EXPERIMENTAL RESULTS

Figure 5 is a photograph of a typical trace of the time variation of the infrared radiation at 4.25 μ. It is observed that the radiation intensity which is proportional to the carbon dioxide concentration, initially increases almost linearly, and after a short time period, the slope increases considerably indicating a very rapid increase in the amount of CO_2 in the system.

A computer program was set up to determine the importance of reactions 15-27 in predicting the curve shown in Figure 5 and other

experiments. In the computer program the carbon monoxide was allowed to react in steps of 0.2% of the initial amount of carbon monoxide in the system. For the range of temperature and pressures employed in this study it was found that reactions 23, 24, 25 and 26 did not appreciably affect the rate of reaction. Furthermore, the depletion of the concentration of CO_2^* by reaction 21 should be a minor contribution when compared with reaction 22. At this point we are left with six possible reactions. It would be impossible to derive all six reaction rate constants from the experimental data. Thus we decided to employ only reactions 15, 16, 18 and 20 in our analysis.

In order to obtain the maximum amount of information from the experimental data it was decided to fit the observed time variation of the intensity of the infrared radiation to a polynomial of the form

$$I = \sum_{n=1} c_n t^n \qquad (27)$$

where

I = intensity in arbitrary units,
t = time in microseconds, and
c_n = the desired coefficients

The order of the polynominal, n, was determined by the best fit to the experimental data. Approximately 20 points were taken from each experimental intensity-time history and were used in the polynomial fit. The best fit normally was obtained for a fourth order (n = 4) for fifth order (n = 5) polynomial.The values of n were varied from 2 to 9 on each set of data.

Polynomial forms were assumed for the CO, CO_2, and O concentrations

$$(CO) = \sum_{n=0} a_n t^n \qquad (28)$$

$$(CO_2) \quad \sum_{n-1} A_n t^n \qquad (29)$$

$$(O) \quad \sum_{n=1} b_n t^n \qquad (30)$$

Steady state concentrations were assumed for (CO_2^{**}), $\frac{d}{dt}\left\{(CO_2^{**})\right\} = 0$. The reaction rate constants were determined by relating the coefficients in Equation (29) to those in Equation (27). The basic procedure is given below.

After several trial and error computations the most promising reaction scheme appeared to be the set of reactions

$$CO + O_2 \xrightarrow{k_{15}} CO_2 + O \qquad (15)$$

$$CO + O \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} CO_2^{**} \qquad (16)$$

$$CO_2^{**} + O_2 \xrightarrow[k_{18}]{} CO_2 + O + O \qquad (18)$$

This set is essentially reactions 15, 16 and 18. The inclusion of additional terms complicated the situation considerably. Employing this system we have

$$\frac{d}{dt}(CO_2) = k_{15}(CO)(O_2) + k_{18}(CO_2^{**})(O_2)$$

and with

$$(CO_2^{**}) = k_{16}(CO)(O)/[k_{-16} + k_{18}(O_2)] = \beta(CO)(O)$$

we obtain

$$\frac{d}{dt}(CO_2) = k_{15}(CO)(O_2) + k_{18}\beta(CO)(O)(O_2)$$

and

$$\frac{d}{dt}(O) = k_{15}(CO)(O_2) - k_{16}(CO)(O) + k_{-16}\beta(CO)(O) + 2\,k_{18}\beta(CO)(O)(O_2)$$

Substituting the polynomial forms [CO], [O] and [CO_2] we can obtain the coefficients, A_n, in terms of the rate constants, β, and the initial amount of carbon monoxide in the system. If we assume that the intensity of the infrared radiation is proportional to the amount of CO_2 in the system then we have

$$I = D(CO_2)$$

and

$$\sum_{n=1} c_n t^n = D \sum_{n=1} A_n t^n$$

Thus we can relate directly the coefficients c_n to A_n if the constant D is known. To remove this ambiguity we decided to relate the coefficients as

$$\frac{c_n}{c_{n-1}} = \frac{A_n}{A_{n-1}} , \qquad (31)$$

since in this manner the constant factor is removed. Thus we have for the reaction mechanism assumed above

$$\frac{2A_2}{(O_2)A_1} = -k_{15} + k_{18}\beta(CO)_i \qquad (32)$$

where $(CO)_i$ is the initial amount of CO in the system. We also have

$$\frac{3A_3}{(O_2)A_2} = \frac{2A_2}{(O_2)A_1} - 2(CO)_i k_{15} k_{18} \beta \left(\frac{(O_2)A_1}{2A_2} \right) \qquad (33)$$

From Equations (31), (32) and (33) we were able to obtain values of k_{15} and k_{18} for all of our experiments.

For all of the different reaction mechanisms which were assumed we obtained the same values of k_{15} within a factor of less than 2. The average values of k_{15} are shown in Figure 7. A least squares fit of these points produces the expression

$$k_{15} = 3.87 \times 10^{9} T^{1/2} \exp(-20{,}900/RT)$$

In several instances both the fourth- and fifth-order polynomials (Equation 27) gave identical results for k_{15}.

The calculated values of $k_{18}\beta$ are shown in Figure 8 from which we obtain

$$k_{18}\beta = 1.04 \times 10^{19} T^{1/2} \exp(-40{,}000/RT)$$

It should be mentioned at this point that in all of the reaction schemes which we tried the second term on the right hand side of Equation (32) always indicated a high activation energy. If we did not assume a steady state concentration of CO_2**, the second term was associated with the formation of CO_2** (Reaction 16). If we did assume a steady state concentration of CO_2** this term was associated with the combined mechanism of obtaining CO_2** and obtaining O through reaction 18 as in the case above.

In the situation in which $k_{18}[O_2]$ is larger than k_{-16} we have

$$k_{18}\beta = \frac{k_{16}}{(O_2)}$$

and we obtain the rate constant k_{16}. The values of k_{16} obtained in this manner are shown in Figure 9, together with the data of Avramenko et al. and Mahan et al. The data of the other investigators indicate a low activation energy (about 3000 cal/mole) while our data indicate a high activation energy (about 40,000 cal/mole). From Figure 9 it would appear that if the value of k_{16} obtained in this manner were the true value in the temperature range 1600 to 2800°K, then the mechanism of reaction 16 apparently must change. Since this possibility seems unlikely, the assumption that $k_{18}(O_2) \gg k_{-16}$ must not be a valid approximation.

If $$k_{-16} \gg k_{18}(O_2)$$

then

$$k_{18}\beta = k_{18}\frac{k_{16}}{k_{-16}} = k_{18}K_{eq,16}$$

where $K_{eq,16}$ is the equilibrium constant for reaction 16, the bimolecular reaction between CO and O. Since it is difficult to obtain an accurate value for this equilibrium constant we cannot obtain an accurate value of k_{18}. However, the activation energy for k_{18} must be the activation energy for $k_{18}\beta$ minus the activation energy for k_{16}, since k_{-16} has no activation energy. In this manner we find that the activation energy for k_{16} must be about 37,000 cal/mole. This value is in good agreement with the 39,000 ± 7000 cal/mole estimated by Sulzmann et al.

In several of our earlier schemes we included reaction 20. The values for all of the rate constants tended to scatter more with the introduction of another variable. However, we found that the ratio k_{20}/k_{18} varied between 4 and 10 for all of our experiments. This approximate value of k_{20}/k_{18} is interesting in that it implies that reaction 20 is not much faster than reaction 18, which requires an activation energy of about 37,000 cal/mole. This result implies that not every collision is effective in deactivating the CO_2** molecule. This conclusion is in agreement with the consideration that reaction 20 should be slow since a spin reversal is involved in the transition of the CO_2** molecule to its ground state.

One factor which may affect our results is the presence of moisture in the system. We have made a concerted effort to eliminate any trace of moisture. However, Brokaw (Ref. 29) has shown that the results obtained by Sulzmann et al. (Ref. 25) and the results presented herein can be explained by eliminating reaction 18 and incorporating reactions 10-15. A trace of moisture as low as 7 ppm would give the same results.

From the point of view of conventional wind tunnels and entry into the Martian atmosphere it appears that reaction 18 may be eliminated in favor of reactions 10-15. However, such a step, although important, requires a knowledge of the amount of moisture in the system. For this reason it may be advantageous to add to all wind tunnel mixtures a certain percentage, for instance, 0.1% moisture, to ensure a uniform mixture.

SECTION VIII

STUDY 2 — SHOCK TUNNEL STUDIES OF CARBON DIOXIDE MIXTURE

The shock tube employed in this study was constructed of stainless steel and had a $3\frac{1}{2}$ inch ID. The driven section was 21 feet long and the driver section was 10 feet long. A nozzle was located between the driven section and a large dump tank. A diagram of the nozzle assembly is shown in Figure 10. The size and placement of the nozzle was such that the gas immediately behind the incident shock wave was passed through the nozzle. Also the reflected shock wave off of the diaphragm should be very weak, if present at all. The nozzle inlet was two inches in diameter. This size permitted only the center core of the gas to go through the nozzle. The gas close to the wall of the shock tube was passed around the nozzle.

The pressure in the nozzle was measured by means of a Kistler Model 603 pressure transducer. A typical pressure trace is shown in Figure 11. The test time appears to be about 400-500 microseconds. In some cases a slight overshoot was noted in the early part of the pressure trace. After considerable effort it was determined that the occasional overshoot was part of the nozzle starting problem. However, after the overshoot had subsided, the pressure remained constant and an accurate value could be obtained.

The measurement of pressure using a pressure transducer requires some type of calibration curve. Normally the manufacturer will supply a calibration curve. However, it is generally unwise to employ such a curve unless it has been checked for validity in the actual rig in which the transducer is to be used. Furthermore, the same electronic cables amplifiers, etc., should be used in the calibration as those employed in the system. For this reason, considerable care was taken to calibrate the pressure transducer mounted in the nozzle. Both argon and argon - carbon dioxide mixtures were used in the calibration process. A typical calibration is shown in Figure 12. It may be noted that the response is quite linear.

SECTION IX

THEORETICAL CONSIDERATIONS

The exact state of the gas can be determined from the axial pressure measurements in the nozzle. To relate the pressure measurements to the state of the gas we must know the relation between these quantities. We have already shown in Figure 1 that for pure carbon dioxide the difference in the pressure computed on the basis of complete chemical

equilibrium and that computed on the basis of frozen flow is considerable. The generation of strong shock waves in pure carbon dioxide requires special driver techniques such as arc-heating or combustion heating. Before we employed these techniques we decided to first investigate a mixture of 80% argon and 20% carbon dioxide. In fact, in some cases, we used a mixture of argon, carbon monoxide, and oxygen to generate the desired mixture.

To predict the "frozen" pressure distribution and the equilibrium pressure distribution it is only necessary to know the state of the gas behind the shock wave. Thus, knowing the temperature, pressure, species concentration, and velocity of the gas, we can determine the Mach number of the gas flow. For all conditions encountered in this study the gas flow behind the shock wave was always supersonic. Thus, knowing these conditions we can predict the axial pressure distribution. A computer program was devised to predict the axial pressure distribution for a gas flow which was chemically frozen in thermodynamic equilibrium.

The determination of the pressure distribution for equilibrium flow was not as simple. Rather than devise a computer program to calculate the properties of the equilibrium expansion it was decided to employ the computer program of Ref. 39, of which we have a copy. This program determines the equilibrium properties of a supersonic expansion but from a given set of stagnation, or chamber, conditions. The program had been used to predict the performances of rocket engines. Thus to determine the equilibrium pressure distribution for our case we have to specify the stagnation conditions. For this purpose we constructed a Mollier diagram for the 80% argon - 20% carbon dioxide which is shown in Figure 13. The stagnation conditions were determined in the following manner. From a knowledge of the temperature and pressure we have a unique value of the enthalpy and entropy. Since the expansion process is assumed to be isentropic, all states of the gas must occur along the vertical line representing a constant value of entropy. Hence, this value of entropy also exists in the stagnation chamber. To determine the value of the stagnation enthalpy we add the value of the enthalpy corresponding to $1/2\ U^2$, where U is the gas velocity, to the static enthalpy of the gas behind the shock wave. Normally we selected several values of enthalpy around the above value. This procedure was followed to minimize the computation time. Next, these several values of stagnation conditions are employed in the NASA program and the nozzle conditions determined for each set. The set which most closely represented the state of the gas behind the shock wave was used to predict the equilibrium pressure distribution down the nozzle. A typical result incorporating both the equilibrium solution obtained by the NASA program and the frozen result obtained by our program is shown in Figure 14.

The pressures obtained in the nozzle should fall somewhere between the equilibrium and frozen values. If the recombination rates are very slow, then the pressures will be close to the frozen values. On the other hand, if the recombination rates are very fast, the pressures will

be close to the equilibrium values. Of course, the terms "slow" and "fast" are relative to the flow process in the nozzle. To predict the pressures for the region between frozen and equilibrium values we must couple the usual flow equations to those governing the finite rate of the chemical reactions. A typical computer program has been developed by Zonars (Ref. 17). Zonars also gives a complete review of all the computer programs which are available for such systems. Dr. Zonars has made his program available for this study. Only minor modifications are necessary.

SECTION X

DISCUSSION OF RESULTS

The calibration of the pressure transducer at the two locations in the nozzle was completed. However, the contract came to an end just prior to the phase during which a detailed experimental program was to be underway. The procedures worked out here should be of value for future work in the expansion of heated carbon dioxide mixtures. Such a study must be undertaken before wind tunnels employing heated carbon dioxide are used on a larger scale. Once the appropriate rates are determined, Zonars' program or a similar program, would provide a means of theoretically predicting the properties of a nozzle flow containing carbon dioxide.

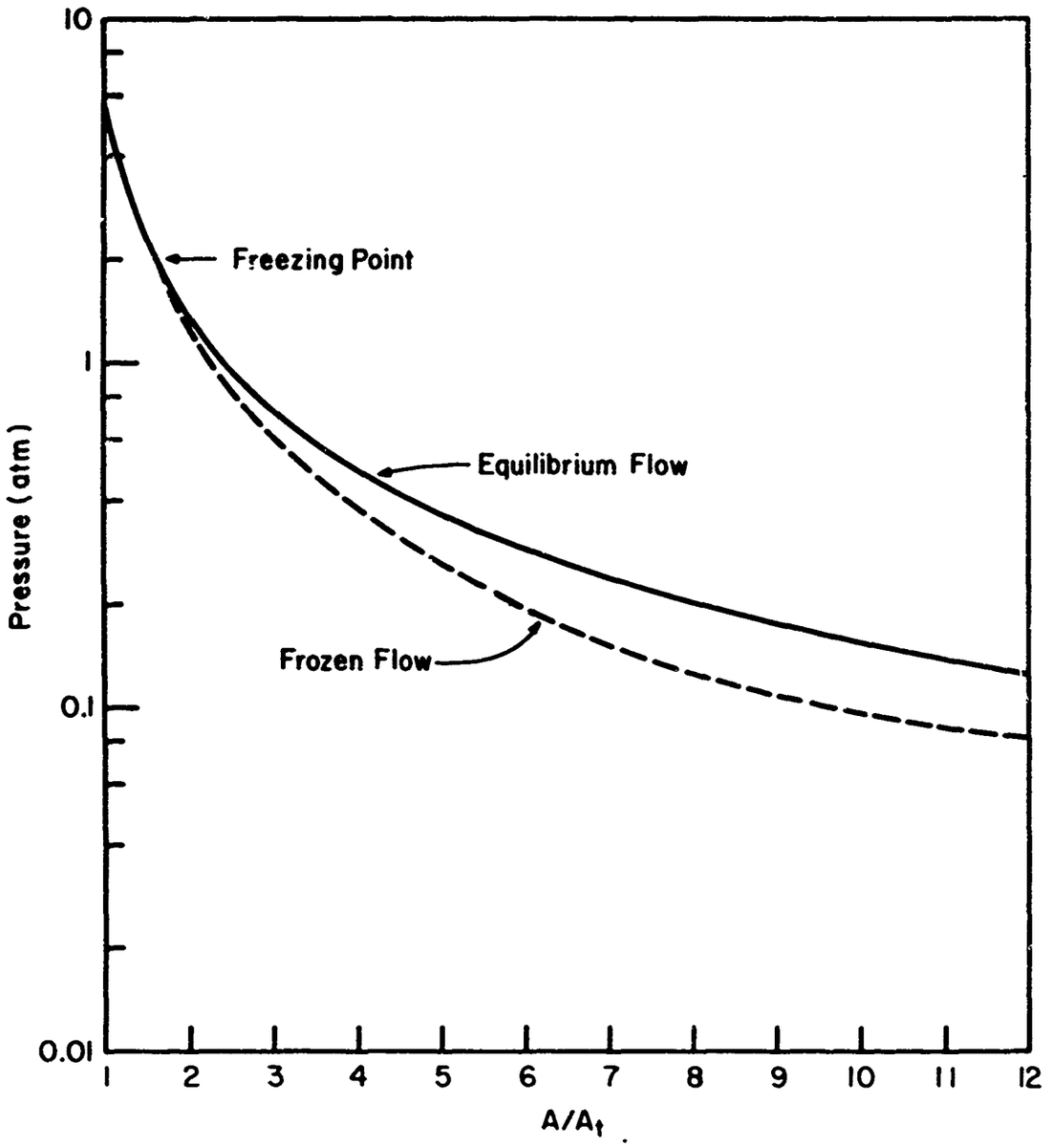


Figure 1 – Pressure Profile for a Supersonic Expansion of Heated Carbon Dioxide for Equilibrium Flow and a Flow Chemically Frozen at M = 1.771. Stagnation Conditions : P = 10.0 atm , T = 4000°K.

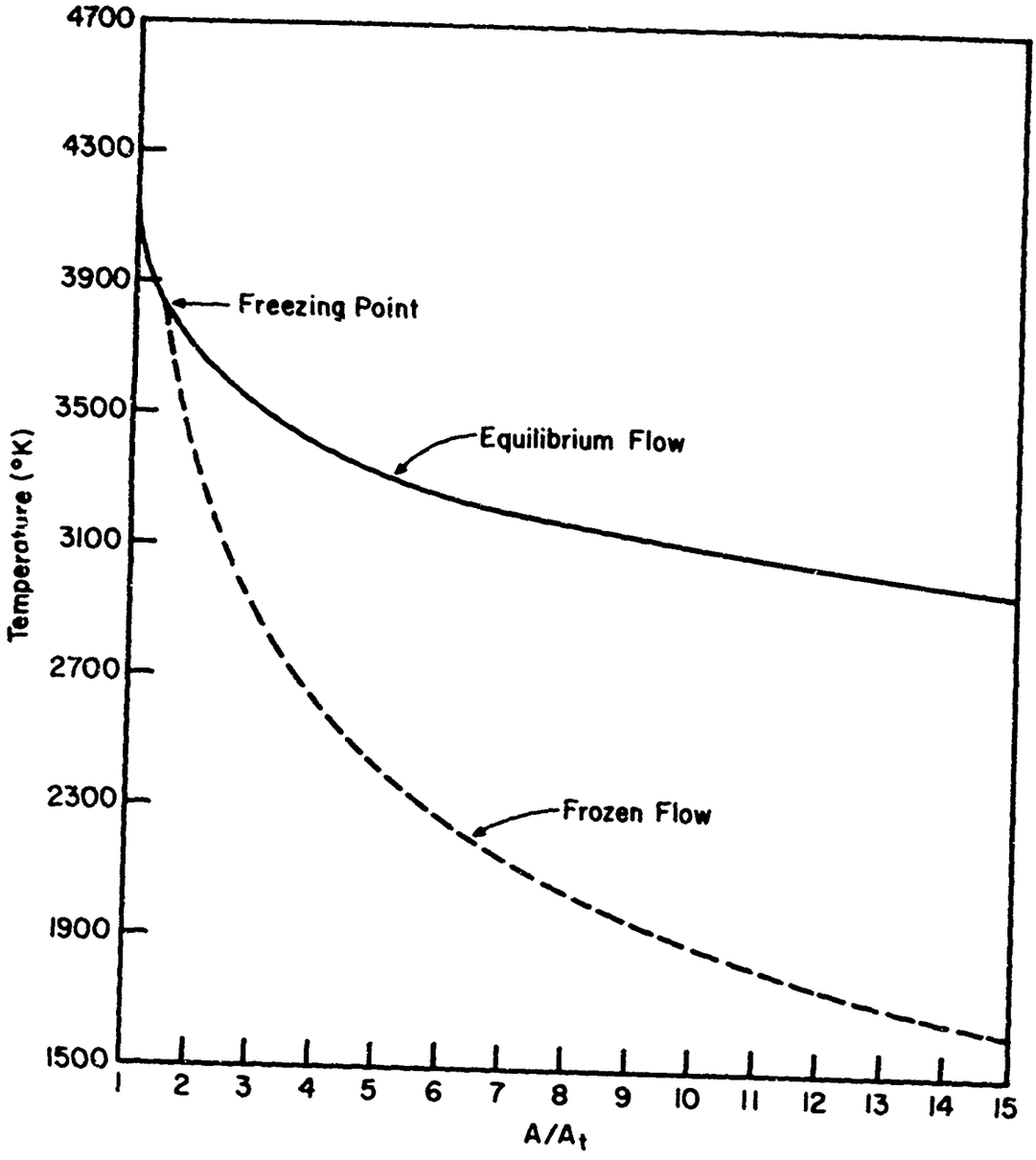


Figure 2- Temperature Profile for a Supersonic Expansion of Heated Carbon Dioxide for Equilibrium Flow and a Flow Chemically Frozen at M=1.771. Stagnation Conditions: P=10.0 atm, T=4000°K.

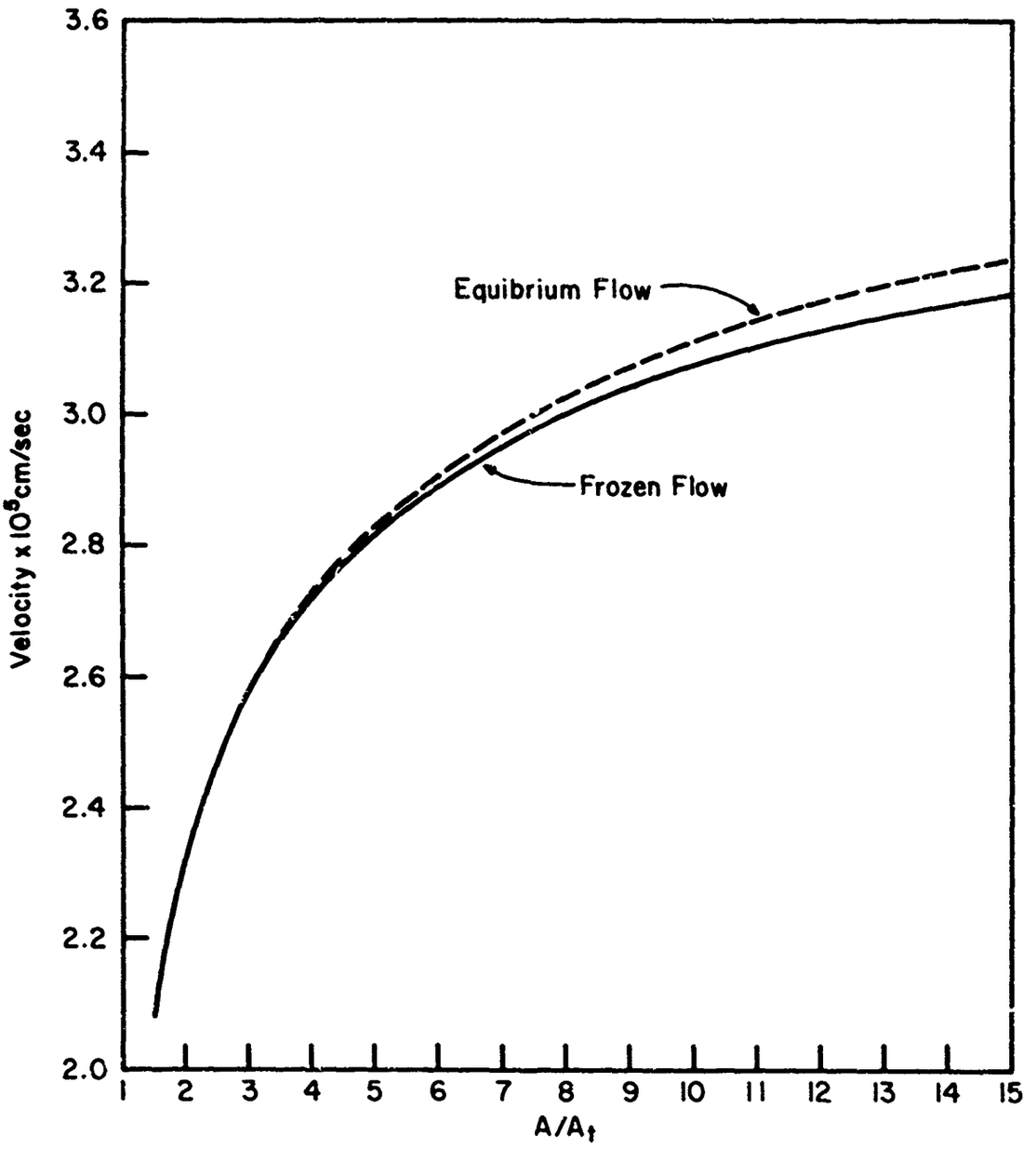


Figure 3 – Velocity Profile for a Supersonic Expansion of Heated Carbon Dioxide for Equilibrium Flow and a Flow Chemically Frozen at M=1.771. Stagnation Conditions: P=10.0 atm, T=4000°K.

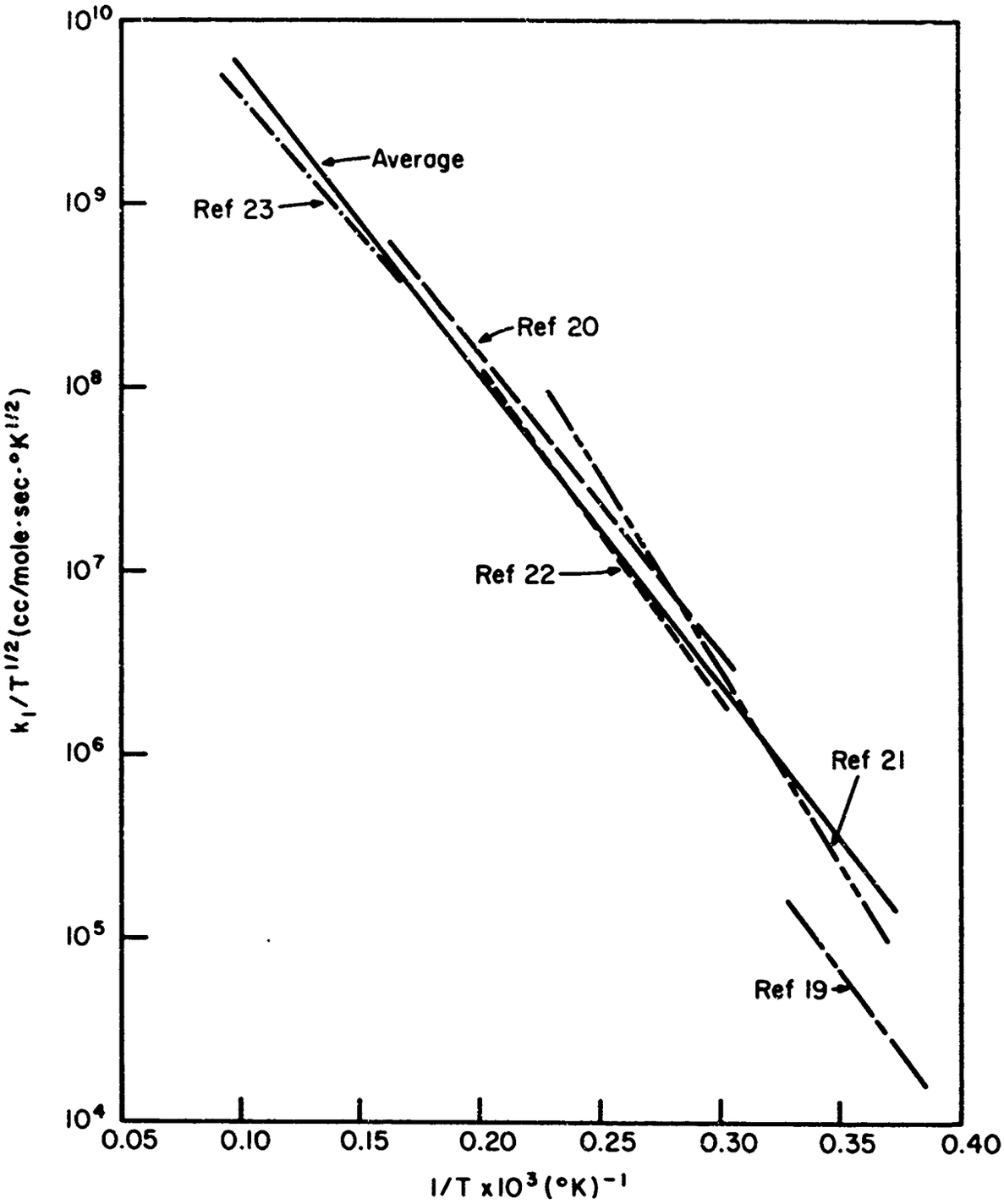


Figure 4 – Experimental Reaction Rate Constants for the Reaction $CO_2 + A \rightarrow CO + O + A$.

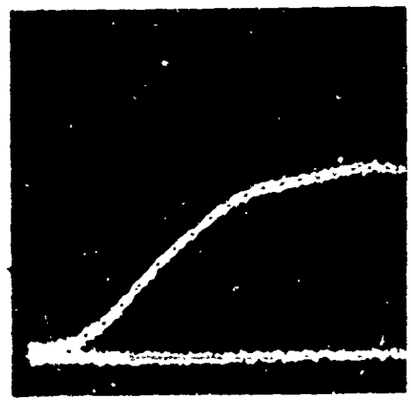


Figure 5 – Time Variation of the Infrared Radiation at 4.25 μ During the Reaction Between Carbon Monoxide and Oxygen. Time is from Left to Right, 30 μsec/div Temperature = 1670° K.

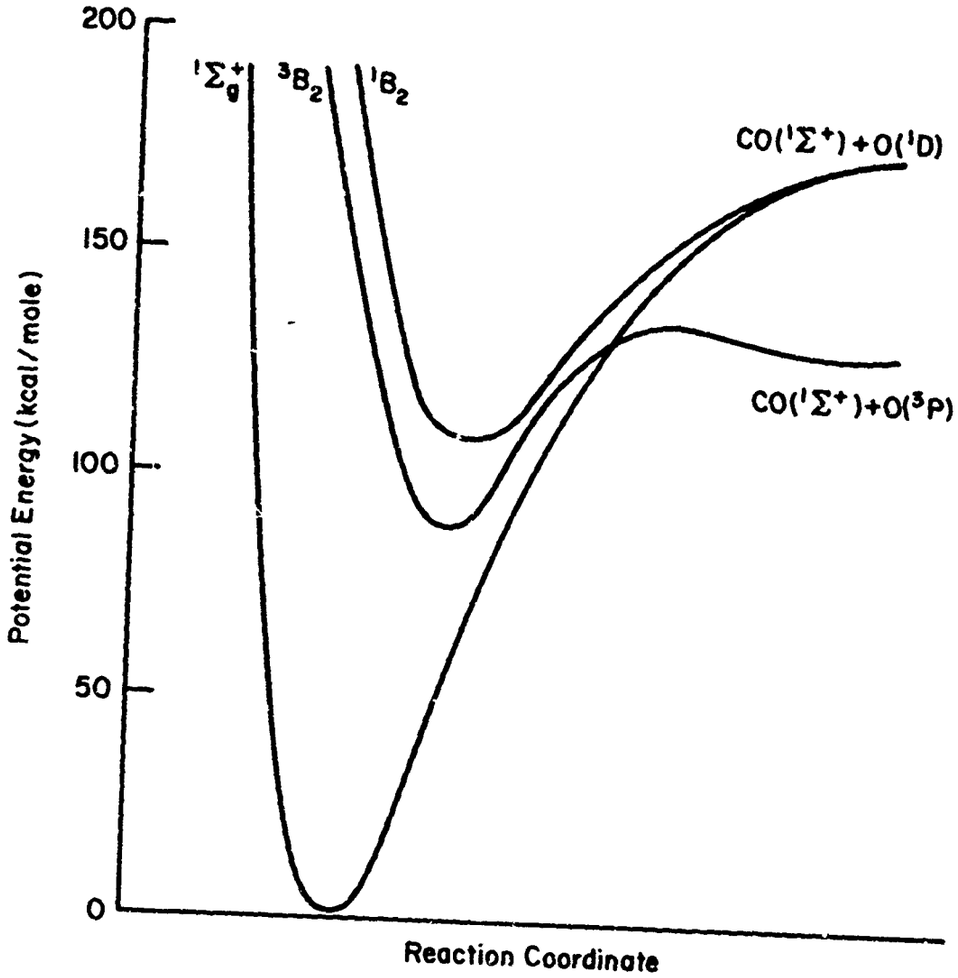


Figure 6–The Electronic States of CO_2.

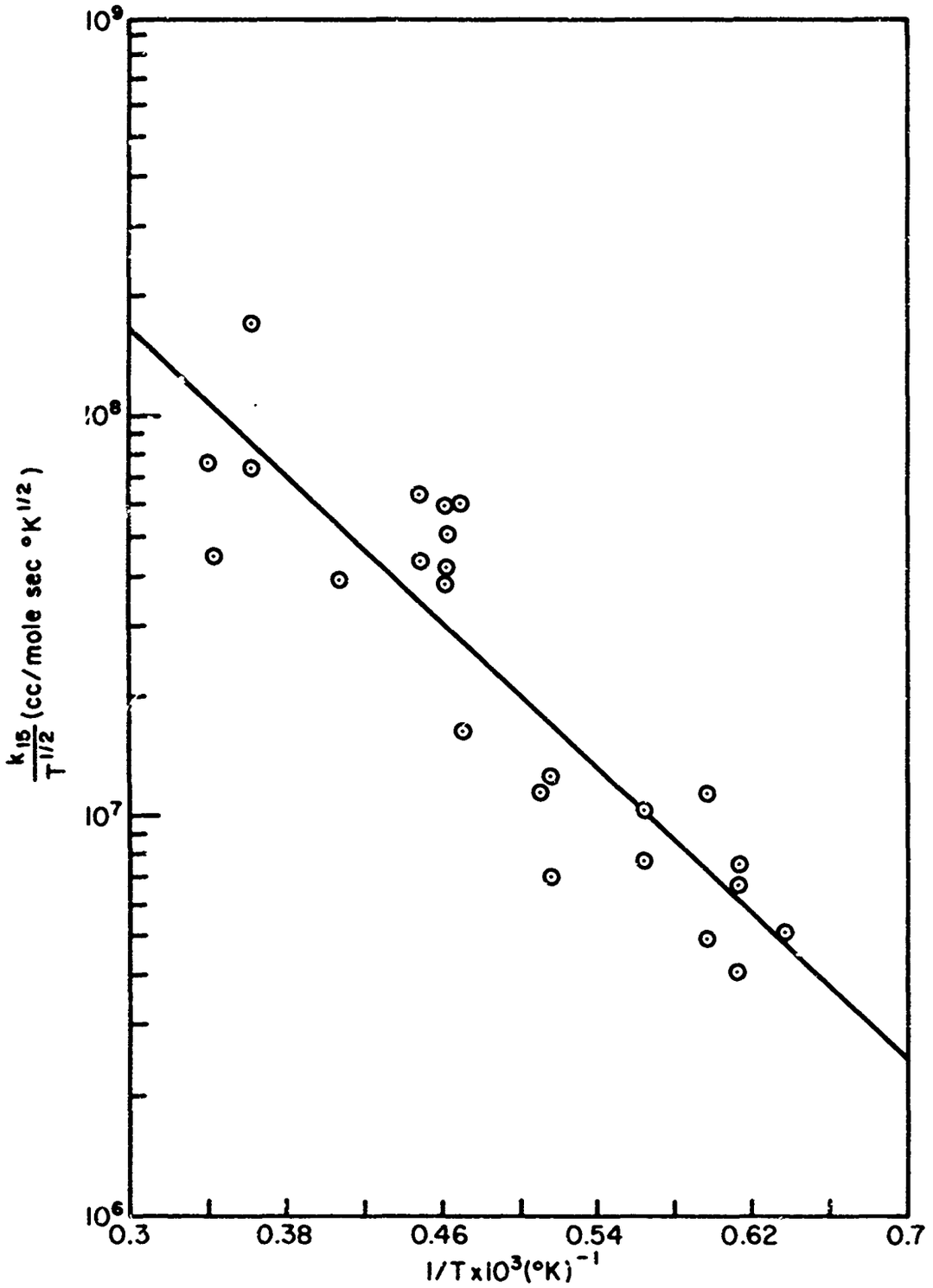


Figure 7–Experimental Values of the Rate Constant k_{15}.

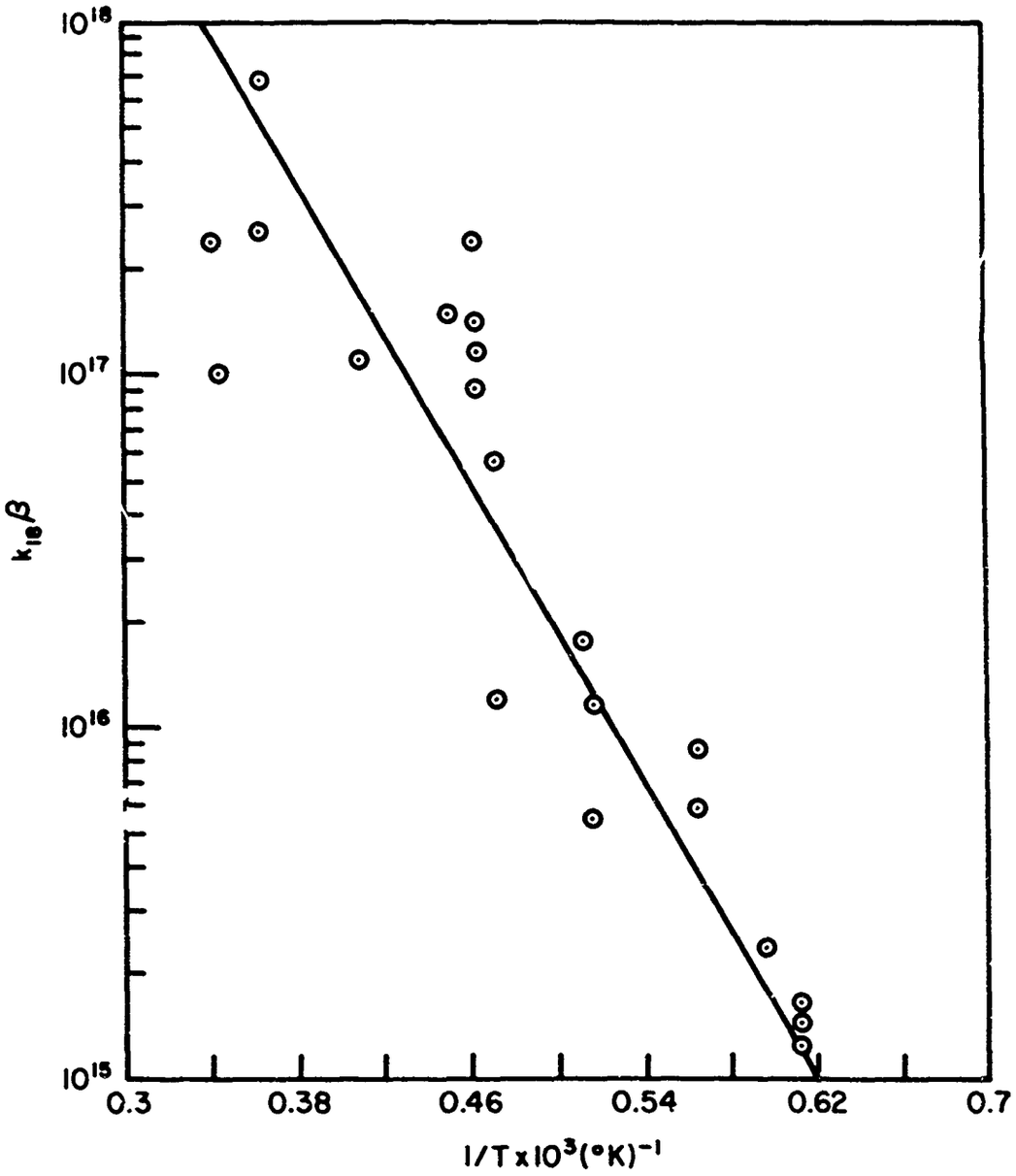


Figure 8–Calculated Values of the Factor $k_{18}\beta$.

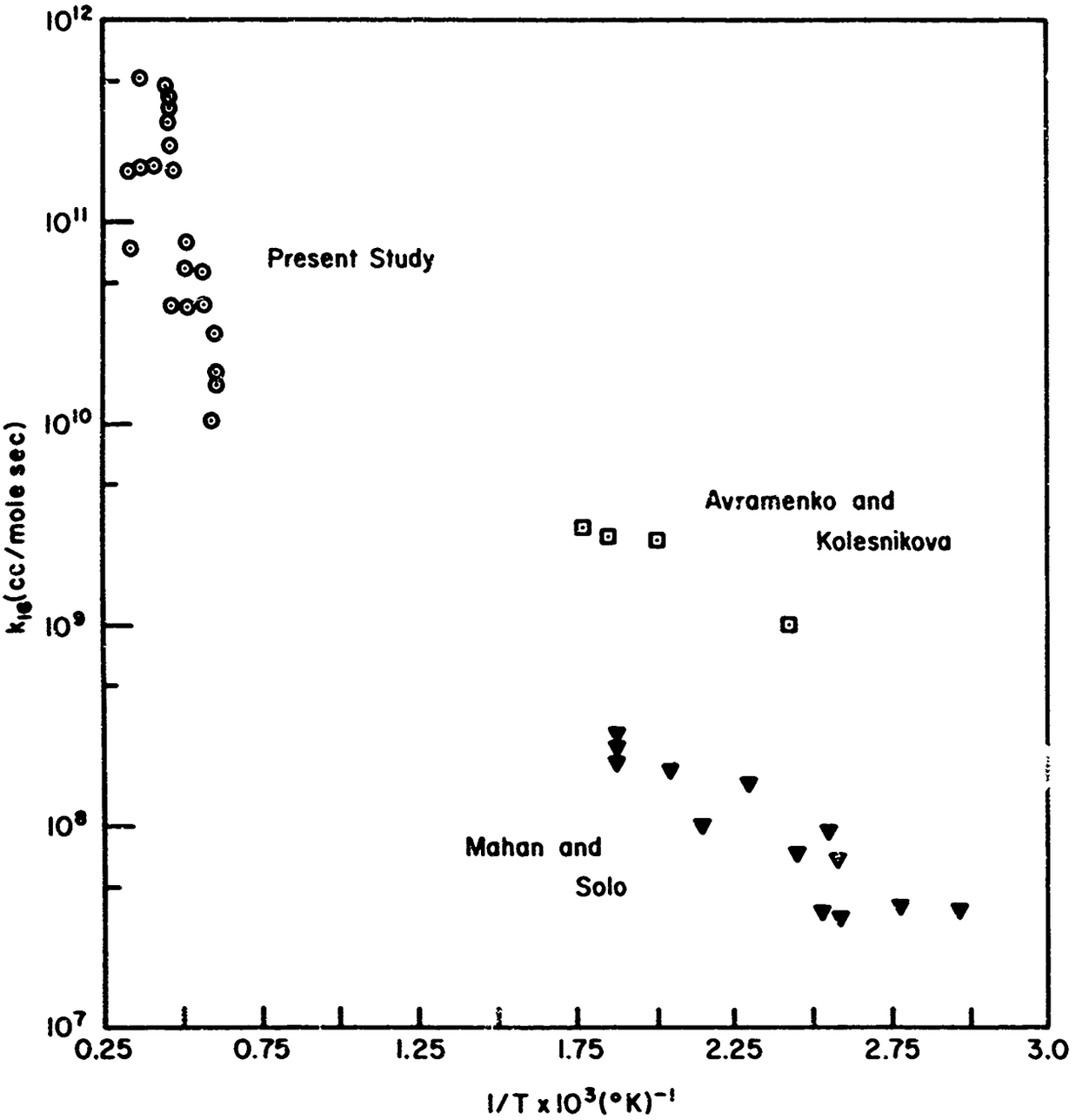


Figure 9– Calculated Values of the Rate Constant k_{16}.

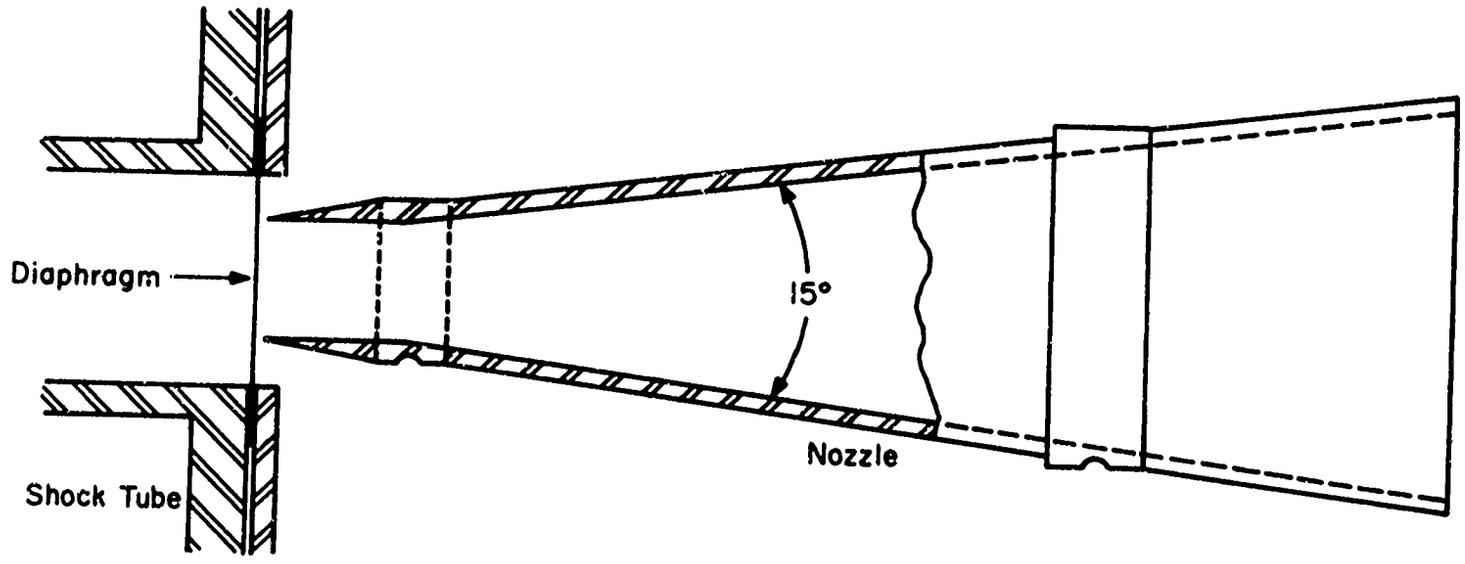


Figure 10 – Schematic Diagram of Nozzle and Shock Tube Assembly.
Nozzle Length 19.59".

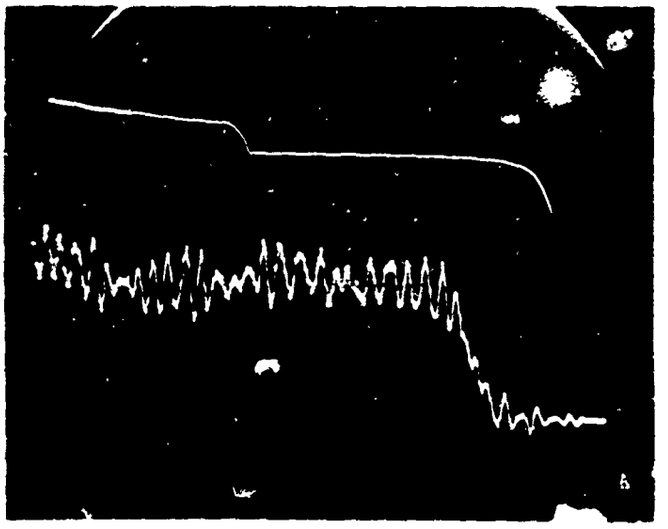


Figure 11 – Measurement of Static Pressure in Nozzle. Upper Trace is Output from Platinum Strips for Velocity Measurement (50 μsec/div). Lower Trace is Output of Pressure Transducer (100 μsec/div).

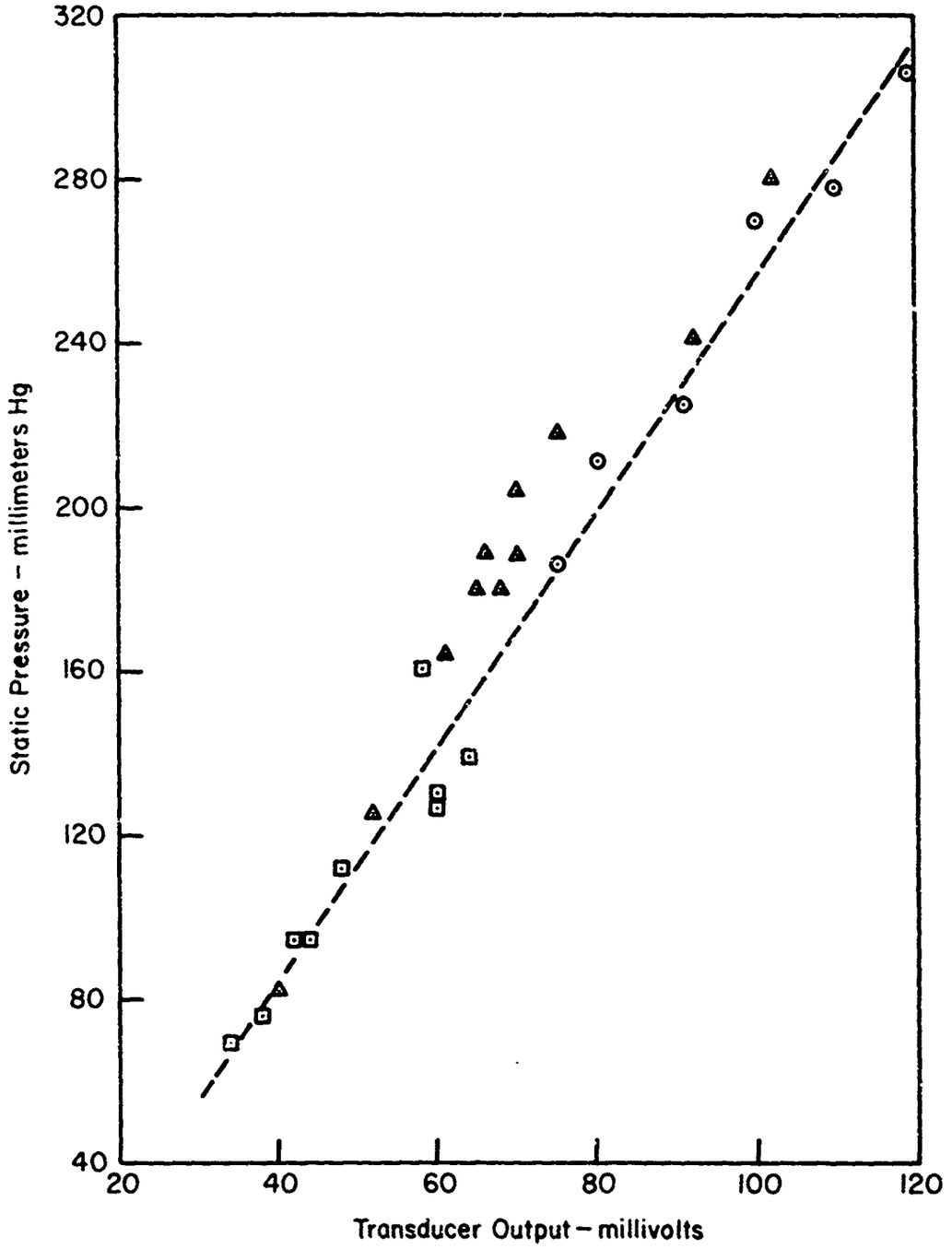


Figure 12– Typical Pressure Calibration of Transducer.

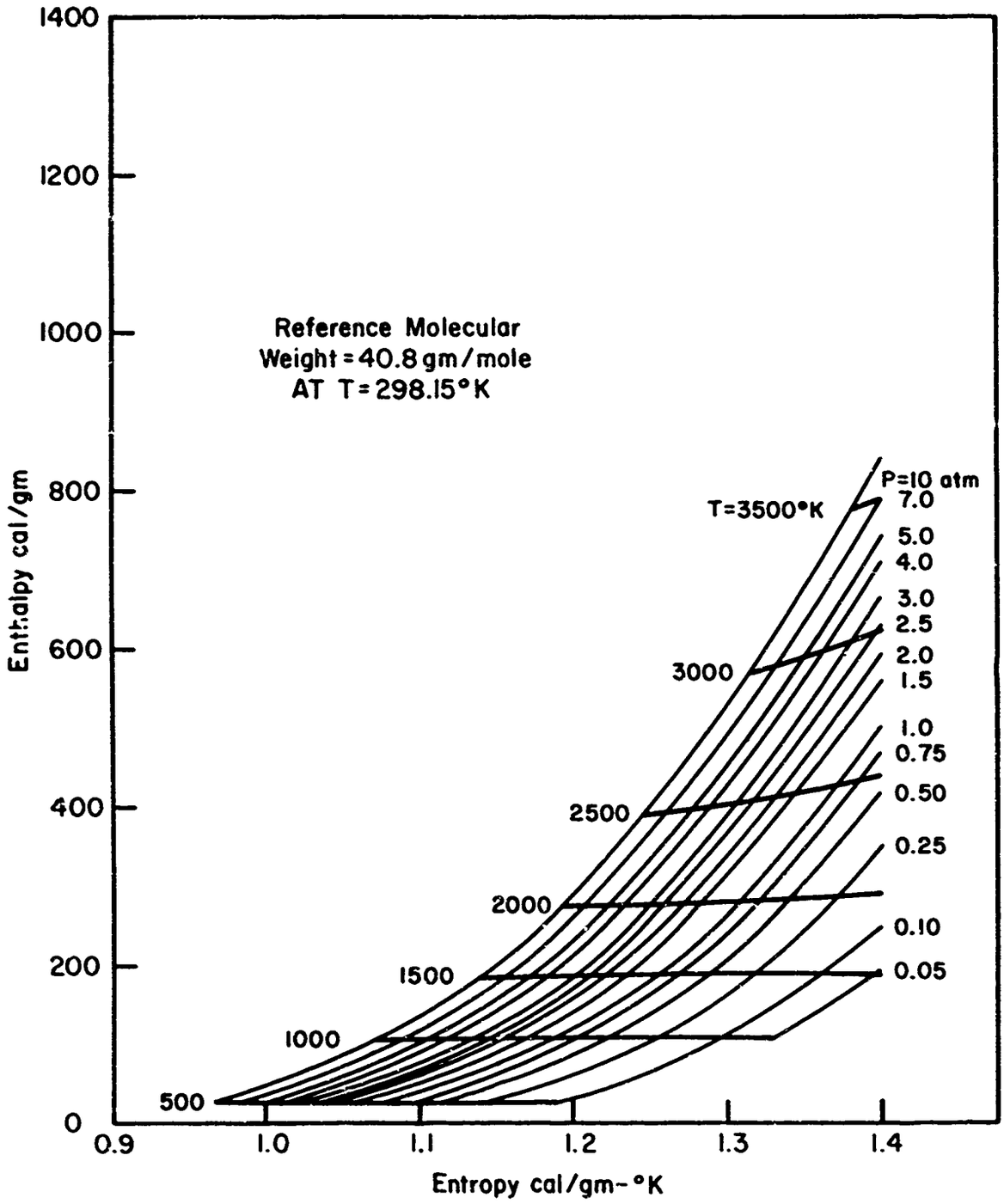
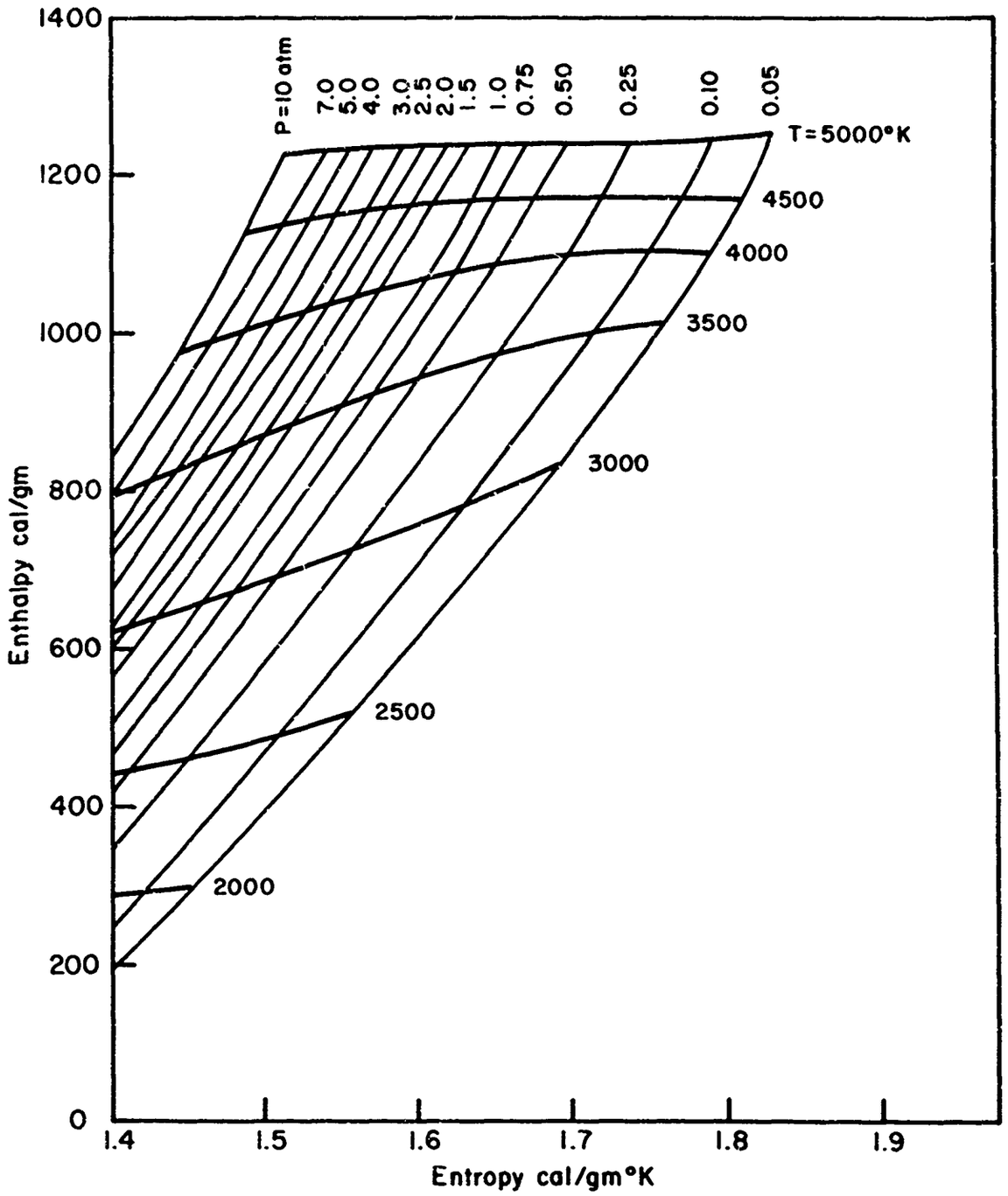


Figure 13- Mollier Diagram for 20% CO_2 - 80% Argon Mixture.



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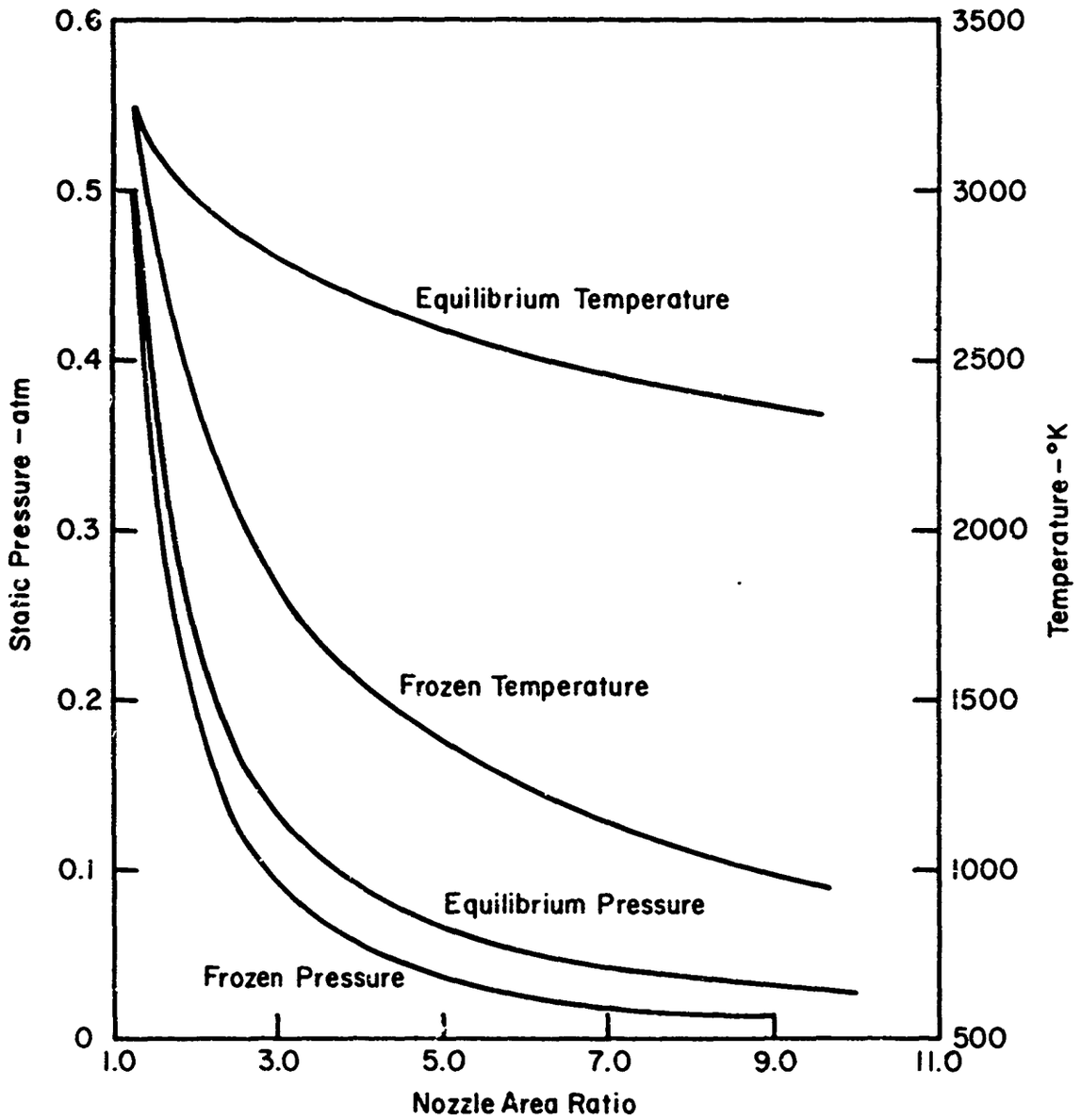

Figure 14 – Calculated Static Pressure and Temperature as a Function of Nozzle Area Ratio for a 20% CO_2–80% Argon Mixture for an Equilibrium and Frozen Expansion. $P_{O_2} = 2$ atm, $T_O = 4500°K$.

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13. ABSTRACT

The reactions between carbon monoxide and oxygen to form carbon dioxide have been examined in two separate experimental studies. In the first study a mixture of carbon monoxide and oxygen was introduced into a shock tube. The mixture then was heated by a shock wave and the rate of formation of carbon dioxide was determined. The carbon dioxide concentration was followed by observing the intensity of the infrared radiation at 4.25μ emitted by the heated carbon dioxide. Rate constants were obtained. However, it was shown that if the amount of water vapor in the system was greater than 7 ppm the primary reactions were governed by the hydrogen-oxygen system of reactions. Hence, it was impossible to obtain reliable rate constants for the CO-O_2 system of reactions. The elimination of such minute quantities of moisture is almost impossible.

The second experimental study involved expanding a high temperature mixture of CO_2, CO, O, and O_2 through a supersonic expansion nozzle. From a measurement of the pressure profile down the nozzle the chemical state of the gas can be determined. Extensive computer programs were formulated for this phase of the investigation. Unfortunately the contract period came to an end at the conclusion of the calibration experiments. Hence, no information was obtained concerning the recombination of carbon dioxide.

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High temperature mixture						
Carbon dioxide						

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