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RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

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RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

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for

Headquarters
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Lunar and Planetary Branch
Washington, D. C.

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FOREWORD

This report was prepared by the IIT Research Institute, Chicago, Illinois, for NASA Contract NASr-65(01). The contract is monitored by Dr. D. Easter of the Lunar and Planetary Exploration Branch, NASA Headquarters, Washington, D.C. The purpose of this program is to provide high temperature properties of simulated atmospheres of Mars and Venus. The present research program includes a measurement of the high temperature emissivity of N_2-CO_2 atmospheres and constituents of these atmospheres, and a measurement of the reaction rates that control the approach to equilibrium behind shock waves in these atmospheres. In this report the dissociation rate of CO for temperatures of 7000°K to 12,000°K is presented. The principal investigator at IIT Research Institute is Mr. William O. Davies. Mr. David A. Gast has assisted in the research, Miss Mary Van Buren has aided in the data reduction, and Dr. S. W. Kash has contributed helpful discussions and suggestions.

Respectfully submitted,

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ABSTRACT

The dissociation rate of CO has been measured for temperatures of 7000°K to 9000°K. The rate of CO disappearance behind shock waves in a CO-Ar gas mixture was monitored by observing the infrared radiation from the CO fundamental vibration band at 4.65 μ. The dissociation rates expressed in an Arrhenius equation and classical collision theory (in cm^3/particles-sec) are, respectively

$$k = (5.80)\ 10^{-12}\ T^{\frac{1}{2}} \exp\ (-\ 8.00\ eV/kT)$$

$$k = (9.38)\ 10^{-13}\ (D/kT)^{3.88} \exp\ (-\ D/kT)$$

where D is the CO dissociation energy, k is the Boltzmann constant and T is the absolute temperature. A rate constant was also determined from observations of emission from the CO (3,0) Triplet band, on the assumption that the population in the $CO(d^3\Delta)_{v=3}$ energy level, excited by collisions of the second kind between $CO(X^1\Sigma)$ molecules and $A(^3P)$ atoms, is proportional to the total CO population. The rates determined from the CO Triplet band emission exhibit a temperature dependence similar to that obtained with the infrared measurements, and are from 20 to 50 percent higher than those given above. Although the analysis of observations made at higher temperatures is complicated by the fact that characteristic relaxation times for CO dissociation and argon ionization are comparable, the expressions above represent an upper limit that is within a factor of two of the rate for temperatures up to 12,000°K.

Abs.

RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

INTRODUCTION

In a continuation of the study of reaction rates behind shock waves in CO_2-N_2 atmospheres, the thermal dissociation rate of CO has been observed for temperatures from 7000°K to 9000°K. The high temperatures were obtained by passing a shock wave through a test gas consisting of two percent CO in Ar. The argon serves as a heat bath, permitting the attainment of high temperatures that are not significantly affected by the chemical reaction being observed. The pressure and temperature of the gas behind the shock wave were obtained from measurements of the initial pressures and shock wave velocities. The rate of disappearance of $CO(X^1 \Sigma^+)$ behind the shock wave was determined by monitoring the CO infrared radiation at a wavelength of 4.65μ, the wavelength at which the CO fundamental vibration band exhibits maximum emission at these temperatures. For the conditions of this experiment the observed infrared emission is directly proportional to the CO concentration, so the dissociation rate can be determined from a characteristic time of the radiation decay.

The emission in the ultraviolet and visible regions of the spectrum was observed for a number of CO electronic transitions which originate on excited triplet energy levels. The population in these triplet energy levels is much higher than would be expected for thermal equilibrium, and it is believed that excitation results from collisions of the second kind between singlet CO molecules and triplet argon atoms. Although the time required for this emission to reach its maximum value is about ten times that of the infrared signal, the ensuing decay of emission intensity occurs at about the same rate as does the infrared signal.

The emission from the CO (3,0) Triplet band at 6433 Å was monitored on each shock wave, and a rate constant determined on the assumption that the collisions of the second kind with argon triplet atoms produce a steady state non-equilibrium population in the CO triplet energy levels that is proportional to the total CO concentration. The fact that the resulting rate constants are only 20 to 50 percent larger than those obtained from the infrared measurements and exhibit approximately the same temperature dependence, suggests that while the approximation used in the analysis is not exactly correct, it is probably not far from the truth, and this triplet band emission could provide a measure of the CO dissociation rate.

The rate constants for both the infrared and CO Triplet band emission are given as functions of temperature and expressed analytically by a least squares fit of the data to both an Arrhenius equation and the classical collision theory. A reliable determination of the rate constant can be made for temperatures up to 9200°K. Beyond that temperature there is some uncertainty concerning the shock wave properties because of the possible influence of argon ionization, which is complicated by the fact that the characteristic relaxation time for argon ionization is comparable to that of CO dissociation. Therefore the analytical expression for the rate constant for temperatures from 7000°K to 9000°K is presented as the most accurate determination possible. The rate constants for temperatures of 9000°K to 12,000°K fall consistently below this curve by at most a factor of two. Thus the rate constant determined for temperatures of 7000°K to 9000°K provides for temperatures up to 12,000°K, an upper limit to the dissociation rate that is met in error by more than a factor of two.

EXPERIMENTAL PROCEDURE

Observations

The measurements of the CO dissociation rate were made with the same shock tube and optical system previously used in the study of CO_2 dissociation.[1,2] The optical system (Fig. 1) consists of a two spectrophotometer channels, permitting infrared and either ultraviolet or visible emission to be monitored on the same shock wave. In both channels the radiation from behind the shock wave is collimated by a pair of slits and directed by mirrors through the appropriate monochromators onto a photomultiplier tube for the ultraviolet-visible channel and an InSb detector for the infrared system. The output signals from these detectors are then displayed on a dual beam oscilloscope, and photographed (Fig. 2).

The infrared signal represents emission from the fundamental vibration band of $CO(X^1\Sigma)$, which is centered at 4.65 μ. When the shock wave passes the slit system there is an initial rapid rise in the infrared emission as the test gas is compressed and heated. Following this rise, there is a nearly exponential decay of emission intensity, which indicates a decrease in the population of excited vibrational levels of $CO(X^1\Sigma)$ and is interpreted as CO dissociation. For the conditions of this experiment, the infrared emission intensity is proportional to the CO concentration. The temperature and pressure of the hot gas depend primarily on the thermodynamic properties of argon and are not significantly affected by the chemical reaction behind the shock wave. The CO

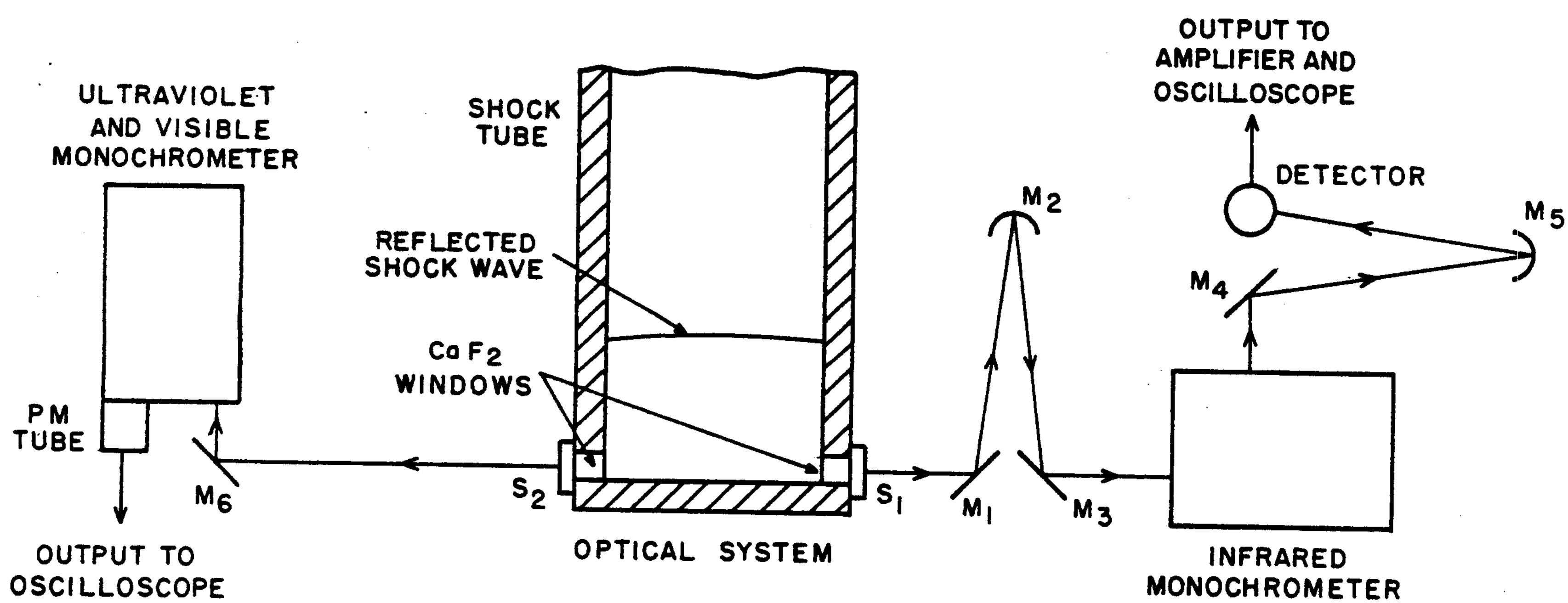
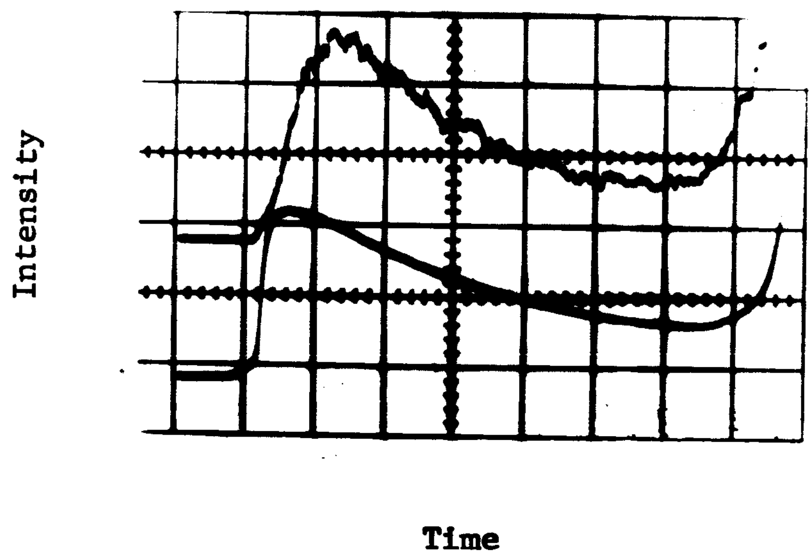


Fig. 1 Optical System



Upper Trace - CO (3,0) Triplet Band

Lower Trace - CO IR Vibration Band

Test Gas - 2% CO, 98% Ar

Temperature = 8300°K ; Pressure = 1 atm

Time Sweep = 50μ sec/cm

Fig. 2 Oscilloscope Trace of Emission Intensity vs. Time optical densities are the order of 0.15 atm-cm, which is well within the region that the CO emission is linear with optical density.

The ultraviolet visible spectrophotometer channel was used to monitor emission from the CO (3,0) Triplet band at a wavelength of 6434 A. Emission from CO electronic band systems is not generally observed in shock heated gases,[3] because thermal equilibrium populations are too low to provide measureable emission. It is known that greater than equilibrium populations in CO triplet energy levels are attained in the presence of a rare gas,[4] and in this investigation the emission from a number of CO bands originating on triplet energy levels has been observed with a gas mixture of two percent CO in argon. The emission profile of the (0,0) (0,1) (0,2) and (0,3) 3 A bands and the (3,0) Triplet band appear very similar, and of these the CO Triplet (3,0) band was selected for further study.

The time required to reach the maximum emission signal for the CO Triplet band is about 50 μ s to 100 μ s longer than for the infrared signal, and is presumably determined by the rates of excitation of $A(^3P)$ atoms and their subsequent collisions of the second kind with $CO(X^1\Sigma)$ atoms. Whatever the excitation mechanism is, the net result is to produce a greater than equilibrium population in the $CO(d^3\Delta)_{v=3}$ energy level, and after reaching a maximum the emission from this energy level decays at approximately the same rate as the infrared emission. The CO triplet band emission was monitored on each shock wave to investigate the possibility of obtaining additional information concerning the CO dissociation.

Data Analysis

The temperatures were calculated on the assumption that the CO translational, rotational and vibrational equilibrium were complete before significant dissociation occurred, and that the ionization of argon does not affect the gas temperature. The characteristic times for CO vibrational relaxation,[5,6] CO dissociation, and argon ionization[7] are shown in Fig. 3. Although CO is noted for its long vibrational relaxation time, the dissociation is sufficiently slow that the asumption above is reasonable. Incomplete vibrational relaxation would not affect the temperature because of the small CO concentration, but it would result in a lower dissociation rate if dissociation from excited vibrational levels is important.

Since the characteristic relaxation times for CO dissociation and argon ionization are the same order of magnitude, at first glance it does not appear possible to calculate the shock wave properties on the assumption that the argon ionization is either negligible or complete at the time the dissociation measurement is made. For that reason, the least squares fit to the data for the dissociation rate constant was accomplished using only the rate constants for temperatures up to 9200°K, for which the effect of argon ionization is negligible.

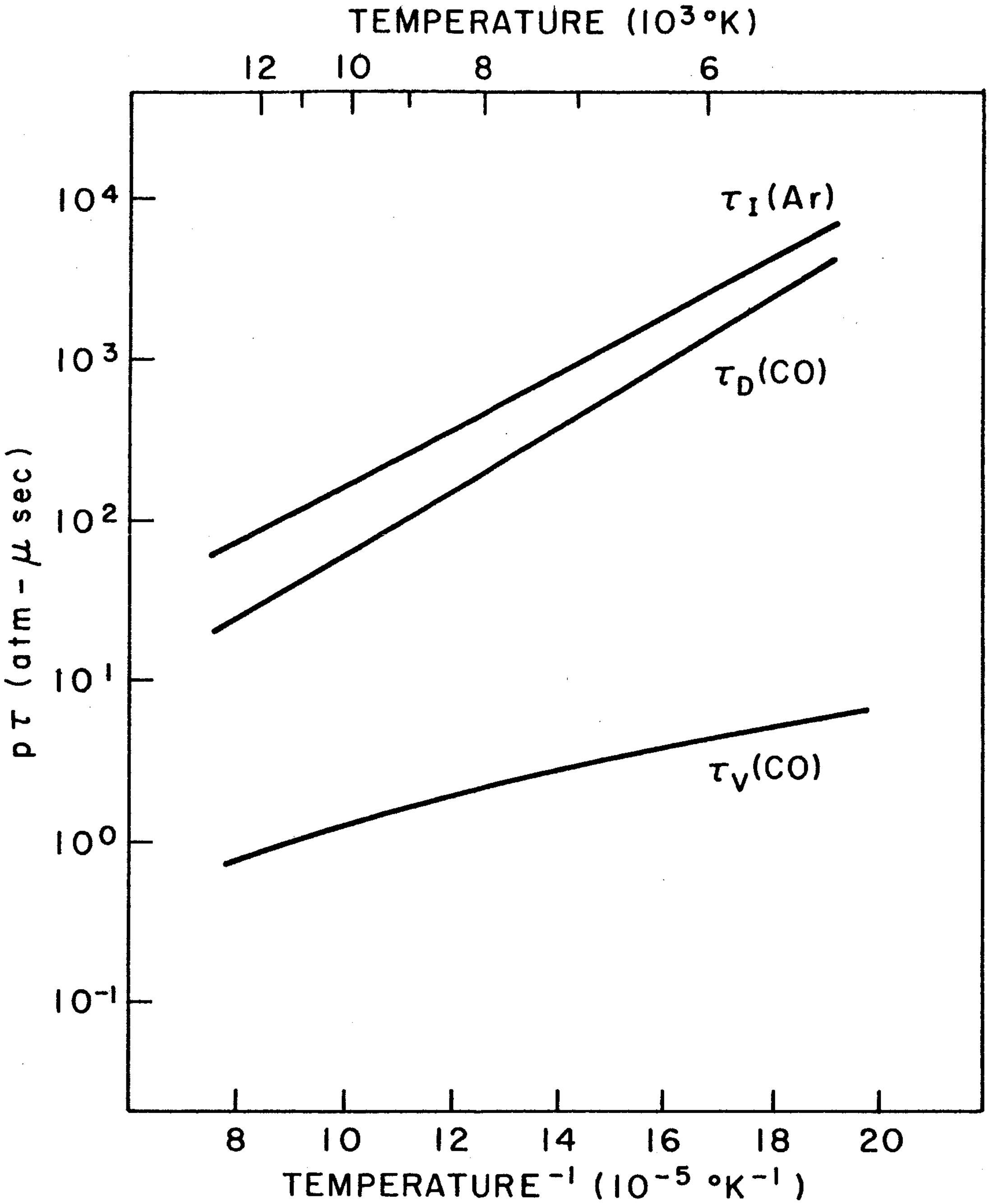


Fig. 3 Characteristic Relaxation Times for Ar Ionization (τ_I), CO Dissociation (τ_D), and CO Vibration, (τ_V).

Since the dissociation of CO and the ionization of argon are occurring simultaneously, there is probably no well defined temperature with which the rate constant can be associated. However, a possible method of data analysis is suggested by a comparison of the character of these two rates, and this method has been used to obtain an indication of the rate at higher temperatures. The argon ionization behind the shock wave occurs in two stages because of the large difference in the relative efficiency of atom-electron collisions as compared to atom-atom collisions. First, there is a very slow increase in ionization presumably resulting from atom-atom collisions, and then as sufficient electrons are produced, the rate increases sharply. On the other hand, the CO dissociation is most rapid just behind the shock wave, since this rate is directly proportional to the CO concentration. Therefore, even though the characteristic times are comparable, it is possible to obtain the measurement of the dissociation rate while the argon ionization is still negligible. This can be expressed quantitatively by noting that the argon ionization is less than 10 percent of its equilibrium value for a time less than 0.4 of the characteristic relaxation time.[7] Thus if the CO dissociation rate measurement is obtained in a time less than 0.4 of the argon ionization relaxation time, the effects of argon ionization are small. The dissociation rates obtained in this way are found to be within a factor of two of the least squares curve for $7000°K \leq T \leq 9200°K$. On the other hand, assuming complete ionization we find rate constants above this least squares curve, which, because of the expected decrease in activation energy with increasing temperature, is taken as an indication that the ionization is not complete when the dissociation measurement is made.

The reaction being observed is $CO + Ar \rightarrow C + O + Ar$, which has a dissociation energy of 11.08 eV. The disappearance of CO is described by the first order reaction $d(CO)/dt = -k(CO)(Ar)$, so the instantaneous CO concentration is given by

$$(CO) = (CO)_o \exp\left[-k(Ar)t\right] \qquad (1)$$

where $(CO)_o$ is the initial CO concentration, (Ar) is the argon concentration, and k is the dissociation rate of CO. Implicit in this expression is the assumption that the CO dissociation is primarily the result of Ar-CO collisions, and that collisions of CO with other atoms and molecules can be ignored because of the low concentration of these species. The dissociation rate is given by

$$k = \ln 2/(Ar)\, t_{\frac{1}{2}} \qquad (2)$$

where $t_{\frac{1}{2}}$ is the half-life for the dissociation reaction. Since the infrared emission intensity is proportional to the CO concentration, this half-life can be determined from a plot of infrared emission intensity vs. time behind the shock waves.

A rate constant was also determined from the CO triplet band emission, on the assumption that this emission is proportional to the total CO concentration. A comparison of the hot gas radiation with a standard radiation source indicates that the hot gas emissivity is less than 0.05, so the gas is optically thin. The assumption on which the data reduction is based is tantamount to postulating a steady-state non-equilibrium population in the $CO(d^3\Delta)_{v=3}$ level that is proportional to the total CO concentration, and therefore decreases at the same rate as the CO dissociation.

The rate constants were fit by the method of least squares to the classical collision theory for diatomic molecules,(8) and to an Arrhenius equation,(9) to provide an analytical description of the rate constant as a function of temperature. According to the classical collision theory the rate of change of CO_2 concentration is

$$-\frac{d(CO_2)}{dt} = ZP\ (D/kT)^S/S!\ \exp(-D/kT) = k(CO_2)(Ar) \qquad (3)$$

where Z is the collision frequency, the steric factor P is the probability that a collision with sufficient energy will produce a dissociation, D is the dissociation energy, k is the Boltzmann constant, T is the absolute temperature and S is a factor that gives the number of transverse translational and internal energy degrees of freedom that contribute energy to the dissociation process. Using the collision frequency from the kinetic theory, the rate constant becomes

$$k = (P\ r^2/S!)(8\pi kT/m)^{\frac{1}{2}}\ (D/kT)^S \exp(-\ D/kT) \tag{4}$$

where r is the effective collision radius and m is the reduced mass of the CO—Ar system. Since the choice of the steric factor P, the collision radius r, and the value of S are uncertain, the rate constants were fit to the equation

$$k = C\ (D/kT)^n \exp(-\ D/kT) \tag{5}$$

to provide the constants C and n, which were then used to calculate S and P.

The factor S is a measure of the degrees of freedom, other than translational along the line of centers, that contribute to the dissociation process. The maximum value of S can be calculated by considering the number of atoms involved in the collision; for a CO-Ar collision, in which angular momentum is conserved, the maximum value is two. Even if this theory were a perfect description of the reaction in other respects, one would expect this value of S to become less than 2 as temperature is increased, because the theory is developed on the assumption that the vibration can be described by a harmonic oscillator. As temperature increases, the effects of anharmonicity are such that less vibrational energy is available than in the harmonic oscillator approximation.

The dissociation rate data were fit to Arrhenius equation of the form

$$k = C\ T^{\frac{1}{2}} \exp(-\ Q/kT) \qquad (6)$$

to determine an activation energy (Q) for the reaction. It is expected that the activation energy will be less than the CO bond dissociation energy of 11.08 eV, because dissociation will occur from excited vibrational levels.

RESULTS AND DISCUSSION

The dissociation rate constants determined from the infrared measurements for temperatures from 7000°K to 9000°K are shown in Fig. 4. The least squares fit of this data to the Arrhenius equation and the classical collision theory yield the expressions (in cm^3/particle-sec)

$$k = (5.80)\ 10^{-12}\ T^{\frac{1}{2}} \exp\ (-\ 8.00\ eV/kT\ ) \tag{7}$$

$$k = (9.38)\ 10^{-13}\ (D/kT)^{3.88} \exp\ (-\ D/kT\ ) \tag{8}$$

respectively.

The activation energy of 8.00 eV is, as expected, lower than the 11.1 eV CO dissociation energy, which is attributed to the relatively high vibrational excitation at these temperatures. This result is consistent with the various theories that suggest dissociation occurs from excited vibrational levels,[10,11,12] but does not provide sufficient evidence to choose among them. According to the classical collision theory, the number of transverse translational and internal energy degrees of freedom that contribute to the dissociation process is $S = n + \frac{1}{2} = 4.38$. For a Co-Ar collision in which angular momentum is conserved the value of S should be ≤ 2, so the results obtained in this investigation suggest this theory is not applicable to CO dissociation. A steric factor of 3×10^{-3} is obtained from the data if the viscosity collision radius is used; this value is

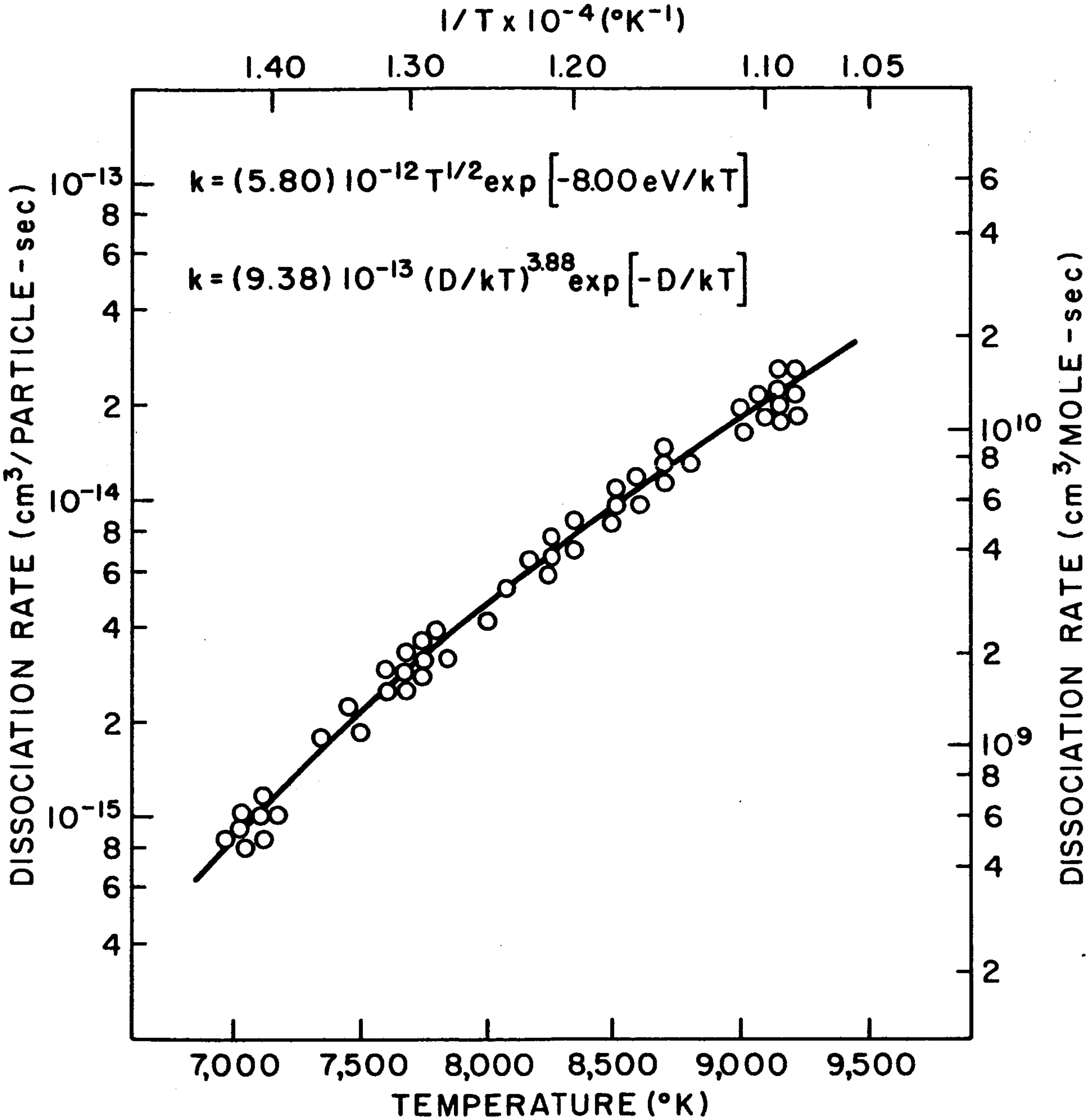


Fig. 4 CO Dissociation Rate vs. Temperature for Temperatures of 7000°K to 9000°K from Observations of Infrared Emission at 4.65 μ .

lower than the values of about 1 to 10^{-2} that are expected if the theory is applicable, which offers a further suggestion that the classical collision theory is not a satisfactory description of CO dissociation.

The rate constants obtained from the CO Triplet band emission over the same temperature range are shown in Fig. 5; the least squares fit of this data to the Arrhenius equation and classical collision theory yield the expressions (in cm^3/particle-sec)

$$k = (4.24)\ 10^{-12}\ T^{\frac{1}{2}}\ \exp\ (-\ 7.58\ eV/kT\ ) \tag{9}$$

and

$$k = (1.98\ 10^{-13}\ (D/kT)^{4.54}\ \exp\ (-\ D/kT\ ) \tag{10}$$

respectively. The activation energy of 7.58 eV is in fair agreement with the 8.00 eV obtained from the infrared observations, which indicates that the temperature variation of these two rates is similar. The dissociation rates obtained from the CO triplet band emission are from 20 to 50 percent higher than the infrared measurements for this temperature range. The application of this data to the classical collision theory yields results similar to the infrared data, in that the value of S = 5.04 is greater than allowed by the physical picture of CO-Ar collisions, and the steric factor of 2 x 10^{-3} is less than expected.

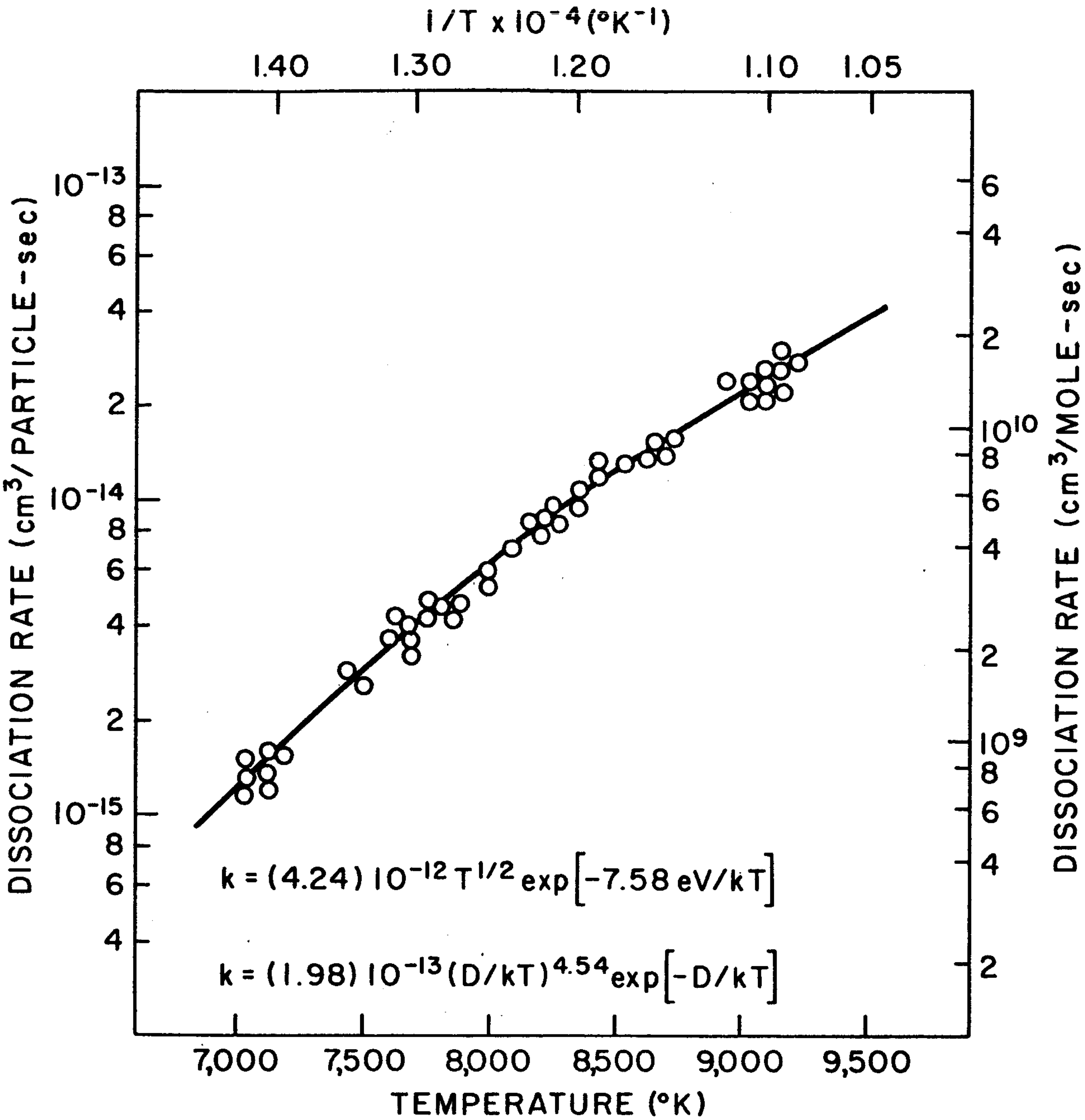


Fig. 5 CO Dissociation Rate vs. Temperature for Temperatures of 7000°K to 9000°K from Observations of CO(3,0) Triplet Band Emission at 6434 A.

A possible interpretation of these results is that the decay of the CO Triplet emission is related to the CO dissociation, but in a more complicated way than the assumption that the population in the $CO(d^3\Delta)_{v=3}$ level is proportional to the total CO population. The excitation of the CO Triplet energy levels probably occurs through collisions of the second kind between $CO(^1\Sigma)$ and $Ar(^3P)$ atoms, following excitation of the argon to triplet levels. Of the three $Ar(^3P)$ levels near 11.5 eV, the $^3P_2$ and $^3P_0$ are metastable while the $^3P_1$ is radiatively connected with the ground state. All three $Ar(^3P)$ levels are within an energy range of 0.17 eV, and since for this experiment $kT \geq 0.5$ eV, it is likely that transitions among these $Ar(^3P)$ states occur so frequently that they may be regarded as one state. If this is the case, the three levels can be considered as one (non-metastable) state, and the concentration of Ar atoms in this "state" is determined by difference between the rate of population by the cascade from higher levels and collisional population of the $Ar(^3P_1)$ level, and the de-population by radiation from the $Ar(^3P_1)$ level and excitation from these three levels.

The concentration in this "state" and the rate of the process involving a collision of the second kind are not sufficiently well known that the assumption of a $CO(d^3\Delta)$ population proportional to the CO concentration can be justified. However, the fact that the rate obtained from these observations is in fair agreement with that obtained from the infrared radiation suggests that this is approximately correct. As far as the reaction rates in CO_2-N_2 atmospheres are concerned, the significance of these results is that the emission profile yields a reaction rate within a factor of two of the CO dissociation rate. This suggests that the CO dissociation could be determined for temperatures at which the reaction cannot be followed by the relatively slow InSb infrared detector.

The observations of CO dissociation rate made at temperatures up to 12,000°K were analyzed on the assumption that the CO dissociation could be measured before the argon ionization affected the temperature. The rates obtained in this manner are shown in Fig. 6, along with an extrapolation to these higher temperatures of the rates (eqns. 7 and 9) determined for $7000°K \leq T \leq 9200°K$. These dissociation rates are everywhere below the extrapolations of the lower temperature rates, by an amount that increases with temperature to a factor of about two at 12,000°K. Although the rate determination at these temperatures is considered less reliable than at lower temperatures because of the uncertainty of shock wave properties, the observed temperature dependence is as expected. If dissociation is more probable from excited vibrational levels,[10,11,12] the activation energy should decrease as the temperature, and therefore vibrational excitation, increases. The difference between the observed high temperature rates and the extrapolations of lower temperature results is approximately the same as observed in other studies.[2]

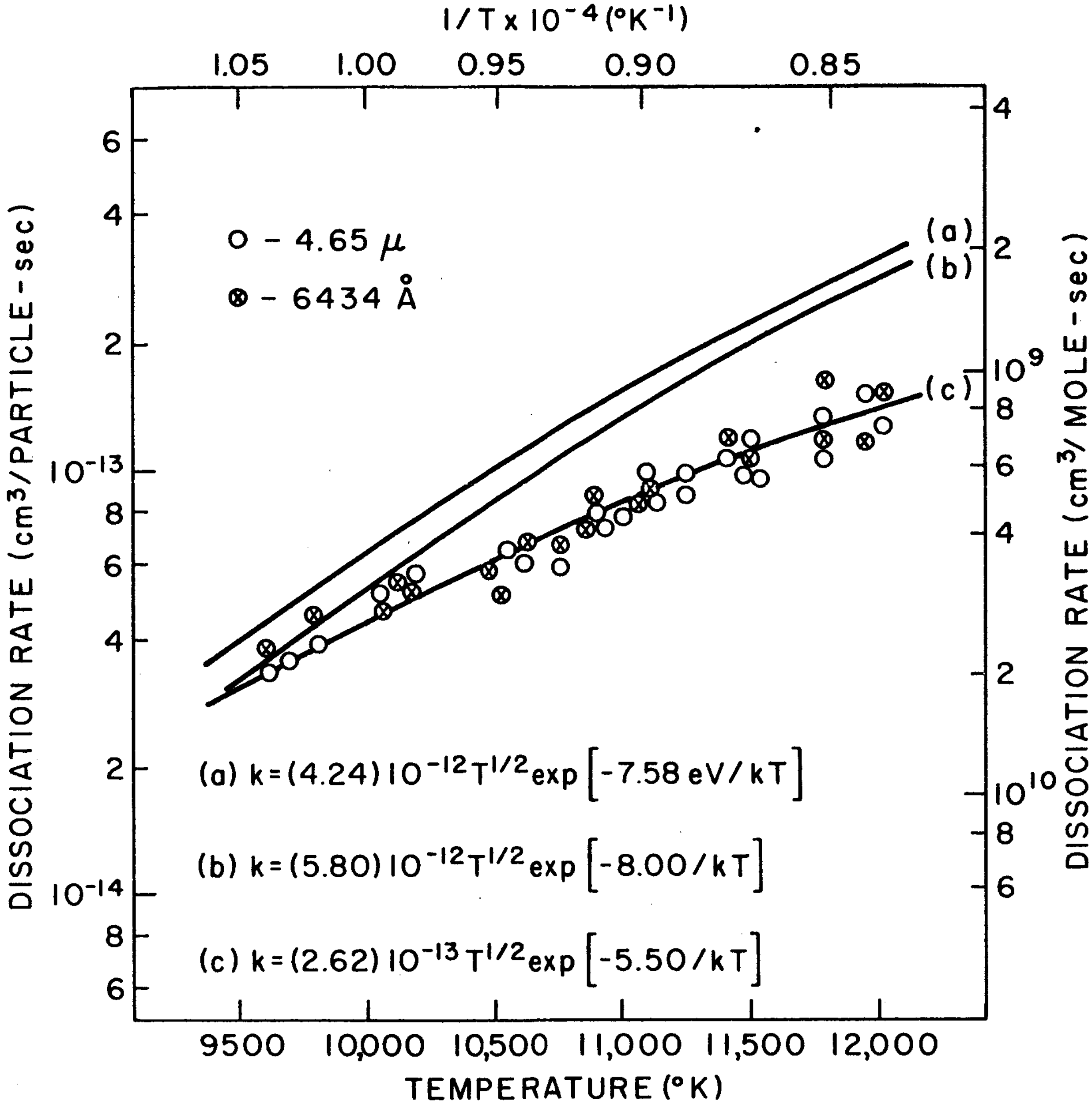


Fig. 6 CO Dissociation Rate vs. Temperature for Temperatures from 9000°K to 12,000°K.

A fit of the higher temperature data ($9500°K \leq T \leq 12{,}000°K$) to the Arrhenius expression yields an activation energy of 5.50 eV and a rate constant of $k = (2.62)\ 10^{-13}\ T^{\frac{1}{2}}\ e^{-\ 5.5\ eV/kT}$. This is presently the best estimate of the CO dissociation rate for $T \geq 10{,}000°K$. The Arrhenius expression for all the observations from 7000°K to 12,000°K is $k = (1.89\ 10^{-12}\ T^{\frac{1}{2}} \exp(-\ 7.2\ eV/kT)$. The expression determined with all the data is not the best fit in any smaller temperature interval, but rather a compromise that provides the best description over the entire temperature range afforded by the Arrhenius equation.

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