N 64 24106
NASA CR 56554

UNPUBLISHED PRELIMINARY DATA

IIT RESEARCH INSTITUTE

formerly Armour Research Foundation of Illinois Institute of Technology

Technology Center Chicago 16, Illinois

CASE FILE
COPY

IITRI-T200-6
(Quarterly Report No. 6)

RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

National Aeronautics and Space Administration

IITRI-T200-6
(Quarterly Report No. 6)

RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

Contract No. NASr-65(01)

Prepared by

William O. Davies

of

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

for

Headquarters
National Aeronautics and Space Administration
Lunar and Planetary Branch
Washington, D. C.

October 1963

FOREWORD

This report was prepared by the IIT Research Institute, Chicago, Illinois, for NASA Contract NASr-65(00). 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_2 for temperatures of 4000°K to 6000°K is presented. The principal investigator at IIT Research Institute is Mr. William O. Davies. Mr. David A. Gast has assisted in the research, Mrs. Elizabeth Isakson has aided in the data reduction, and Dr. S. W. Kash has contributed helpful discussions and suggestions.

Respectfully submitted,

IIT RESEARCH INSTITUTE

William O Davies

William O. Davies, Research Physicist
Plasma and Electron Physics Research

APPROVED BY:

SW Kash

S. W. Kash, Manager
Plasma and Electron Physics Research

B. M. McCormac,
Associate Director
of Geophysics Division

ABSTRACT

The dissociation rate of carbon dioxide has been determined for temperatures from 3500°K to 6000°K. The rate of disappearance of carbon dioxide behind shock waves in CO_2-N_2 and CO_2-Ar gas mixtures was monitored by observing the radiation from the CO_2 4.3μ fundamental vibration band. The dissociation rates obtained for one percent CO_2 in both argon and nitrogen were fit to the classical collision theory for diatomic molecules, yielding the rate constants

$$k_{Ar} = (9.71)\ 10^{-14}\ (D/kT)^{4.38}\ \exp(-\ D/kT)$$

$$k_{N_2} = (3.27)\ 10^{-14}\ (D/kT)^{4.72}\ \exp(-\ D/kT)$$

in units of cm^3/particles-sec. It was also found that the dissociation rate is not altered within the experimental error by (a) increasing the CO_2 concentration up to ten percent, (b) adding either CO or H_2O to the gas for concentrations of these gases up to two percent, (c) making the dissociation measurement at different wavelengths or pass bands within the 4.3μ band, or (d) making the dissociation measurement by observing the radiation from the CO_2 2.7μ combination bands. The activation energy, Q, for the reaction determined with an Arrhenius plot of $kT^{-1/2} = P \exp(-\ Q/kT)$, was found to be 3.24 eV. This value is considerably less than CO bond energy of 5.45 eV, which indicates that the dissociation process involves other than just ground state species.

RADIATIVE ENERGY TRANSFER ON ENTRY INTO MARS AND VENUS

I. INTRODUCTION

The results of an investigation of the thermal dissociation of carbon dioxide are presented in this report. The dissociation rate of carbon dioxide is important in the quantitative assessment of radiative energy transfer in CO_2-N_2 atmospheres because some of the strongest emitters, such as CN and C_2, are formed by recombination of N_2 and CO_2 dissociation products. The thermal dissociation rate of carbon dioxide has been determined in the temperature range from 3500°K to 6000°K for small concentrations of CO_2 in both argon and nitrogen. The high temperatures were obtained by passing a shock wave through the test gas, using the experimental system previously described in the study of CO_2 emissivity.[1] The argon and the nitrogen serve as a heat bath permitting attainment of high temperatures that are not significantly affected by the chemical reaction behind the shock wave. The pressure and temperature behind the shock wave were obtained from measurements of initial pressures and the shock wave velocities. The experimental system and the method of data analysis are described in Appendix I.

The rate of disappearance of CO_2 ($X\Sigma^1$) behind the shock wave was determined by monitoring the infrared radiation from the CO_2 4.3μ fundamental vibration band. The observed emission could conceivably depend on the gas temperature and pressure, and the optical density of CO_2 and any other infrared active gases that are present. The temperature and

total gas pressure are essentially constant for the dilute CO_2 concentrations used, as these gas properties are determined primarily by the argon and nitrogen. By reference to the CO_2 emissivity data previously obtained[2] it can be seen that the emission signal is independent of total pressure and linearly dependent on the CO_2 optical density for the pressure and optical densities considered. The only infrared dissociation product that could seriously affect these measurements is carbon monoxide. A wavelength of 4.45 μ was selected to provide a large ratio of CO_2 to CO emission, and the measurements were made just behind the shock wave where the CO concentration is low.

Most of the dissociation rate data were obtained with a gas mixture of one percent CO_2 in either argon or nitrogen, and at a wavelength of 4.45 μ with an 0.05 μ band pass. Additional data were obtained to determine the effects of

(a) variation of the CO_2 concentration from one-half percent to ten percent,

(b) the presence of H_2O for concentrations up to two percent,

(c) the presence of CO for concentrations up to two percent, and

(d) variation of wavelength and band pass within the 4.3 μ CO_2 band.

The dissociation rate was also determined from observations of emission from the 2.7 μ combination bands of CO_2. None of these variations in gas mixture or experimental procedure affected the rate constants within the experimental error.

The decrease in CO_2 concentration is described by the first order reaction equation

$$d(CO_2)/dt = - k_M(CO_2)\ (M) \tag{1}$$

where k_M is the rate constant, (CO_2) is the carbon dioxide concentration, and (M) is the argon or nitrogen concentration. The instantaneous CO_2 concentration is then given by

$$(CO_2) = (CO_2)_o \exp\left(- k_M(M)t \right) \tag{2}$$

and the rate constant is obtained from the expression

$$k_M = \ell n2/(M)\ t_{1/2} \tag{3}$$

where $t_{1/2}$ is the half-life obtained from a plot of emission intensity vs. time. The rate constants for CO_2 dissociation are given as a function of temperature, and determined analytically by a least squares fit of the data to (a) the classical collision equation for diatomic molecules[3] and (b) an Arrhenius equation.[4] The classical collision theory yields an expression of the form

$$k_M = C(D/kT)^n \exp(- D/kT) \tag{4}$$

where D is the dissociation energy, k is the Boltzmann constant, and T is the absolute temperature. In this theory the factor n is a measure of the internal and transverse translational degrees of freedom that contribute to

the dissociation process, and the constant C is proportional to the number of collisions that are effective in producing dissociation. The Arrhenius equation

$$k = P\ T^{1/2} \exp(-\ Q/kT) \tag{5}$$

was used to determine an activation energy (Q) for the process.

The dissociation rate constants for CO_2 with both argon and nitrogen as collision partners are given, and the results are compared to the classical collision theory. The activation energy and rate constants obtained in this experiment are compared to the results of a study of CO_2 dissociation conducted at lower temperatures.[5]

II. RESULTS

The dissociation rate constant is shown as a function of temperature for the one percent CO_2 mixture in argon in Fig. 1, and for the one percent CO_2 in nitrogen in Fig. 2. The least squares fit of these data to the classical collision theory (eqn. 4) yields the rate constants

$$k_{Ar} = (9.71)\ 10^{-14}\ (D/kT)^{4.38}\ \exp(-\ D/kT) \qquad (6)$$

and

$$k_{N_2} = (3.27)\ 10^{-14}\ (D/kT)^{4.72}\ \exp(-\ D/kT) \qquad (7)$$

(in cm^3/particles-sec) for the argon and nitrogen, respectively, as collision partners.

According to the classical collision theory the number of transverse translational and internal energy degrees of freedom that contribute to the dissociation process is $S = n+1/2$. The maximum value for S can be calculated by considering the number of atoms and degrees of freedom involved in the collision. For a CO_2-Ar collision the maximum value is six if rotation is included and five if it is not; for the N_2-CO_2 collisions the corresponding numbers are eight and six. (At high temperatures these maximum values of S would be lower, as the classical collision theory neglects the anharmonicity of vibrational energy). The values of S obtained from the least squares fit of the data to eqn. 4 are 4.88 and 5.22 for argon and nitrogen respectively, as collision partners. Despite the inherent limitations of the theory both of these values are physically reasonable, and a possible interpretation is

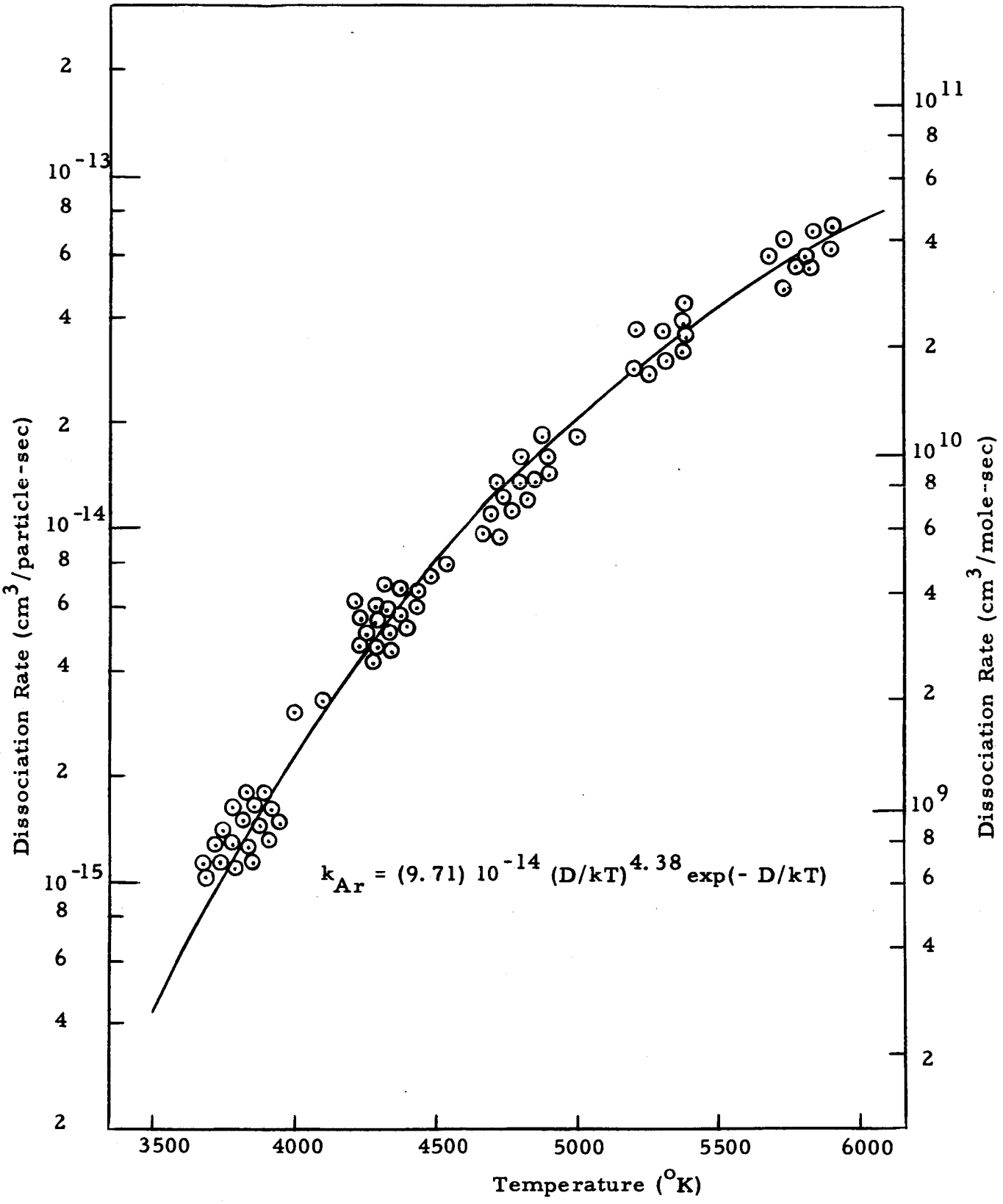


Fig. 1 Dissociation Rate of CO_2 vs. Temperature for One Percent CO_2 in Argon

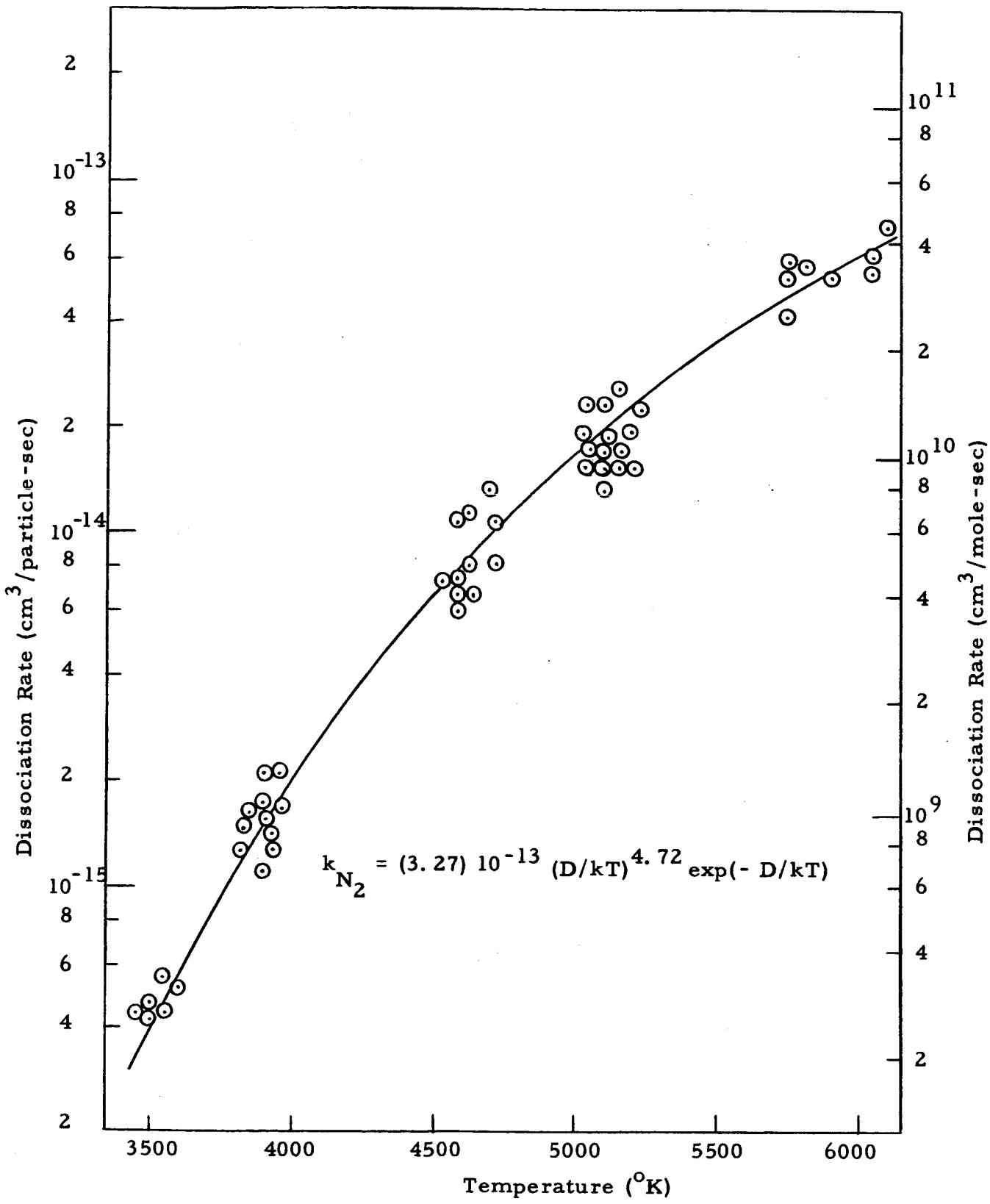


Fig. 2 Dissociation Rate of CO_2 vs. Temperature for One Percent CO_2 in Nitrogen

as follows. For the argon-CO_2 collisions the conservation of angular momentum rules out the use of rotational degrees of freedom, but nearly all of the vibrational and transverse translational energy is utilized in the dissociation. The higher value of S obtained with the CO_2-N_2 gas mixture could be explained by the utilization of rotational energy. The vibrational energy of N_2 is probably not changed significantly during the collision, so that only the vibrational energy of the dissociating molecule contributes to the dissociation. For the N_2-CO_2 collision the exchange of rotational energy is allowed, and the result suggests that one square term of the rotational energy is used. If the energy of transverse translation, CO_2 vibration, and one rotation are used, the classical value of S for the CO_2-N_2 is 5-1/2. When allowance is made for the anharmonicity of potential energy and the experimental error, this is in agreement with the measured value of S = 5.22.

The other constant (C) obtained from the least squares fit of the data can be used to calculate the steric factor P, which is the fraction of sufficiently energetic collisions that yield a dissociation. If the collision radii from viscosity measurements[6] are used the steric factors are 4.8×10^{-3} for CO_2-Ar and 5.4×10^{-3} for CO_2-N_2, which indicates that about five in every thousand collisions is successful in dissociating a CO_2 molecule.

The use of this expression provides a convenient empirical description of the dissociation rate of CO_2 over the temperature range considered, but the physical picture of the collision process should not be over emphasized. The intention is to obtain an accurate analytical description of the disappearance of CO_2, and for this purpose the classical collision theory will suffice.

The dissociation rate of CO_2 was also determined for

(a) CO_2 concentrations of one-half, two, five and ten percent CO_2 in argon,

(b) H_2O concentrations of one-half and two percent with one percent CO_2 in argon,

(c) CO concentrations of one-half and two percent with one percent CO_2 in argon, and

(d) one percent CO_2 in argon at wavelengths of 2.7μ and 4.8μ.

The dissociation rates determined for these cases are shown in Fig. 3, along with the least squares curve (eqn. 6) for the dissociation rate constant of the one percent CO_2 in argon at 4.45μ. Each point on this graph is the average of five measurements, and the vertical lines represent the maximum and minimum values of the rate constant for the five measurements. These results indicate that the dissociation rate is not significantly affected by small concentrations of H_2O and CO, and is essentially the same for measurements made at different wavelengths and pass bands within the 4.3μ CO_2 band and for the 2.7μ combination bands.

The Arrhenius plots are shown in Figs. 4 and 5 for one percent CO_2 in argon and nitrogen, respectively. The least squares fit of the data (eqn. 5) yields

$$k_A = (4.79)\ 10^{-13}\ T^{1/2} \exp(3.24\ eV/kT) \qquad (8)$$

and

$$k_{N_2} = (4.07)\ 10^{-13}\ T^{1/2} \exp(3.23\ eV/kT) \qquad (9)$$

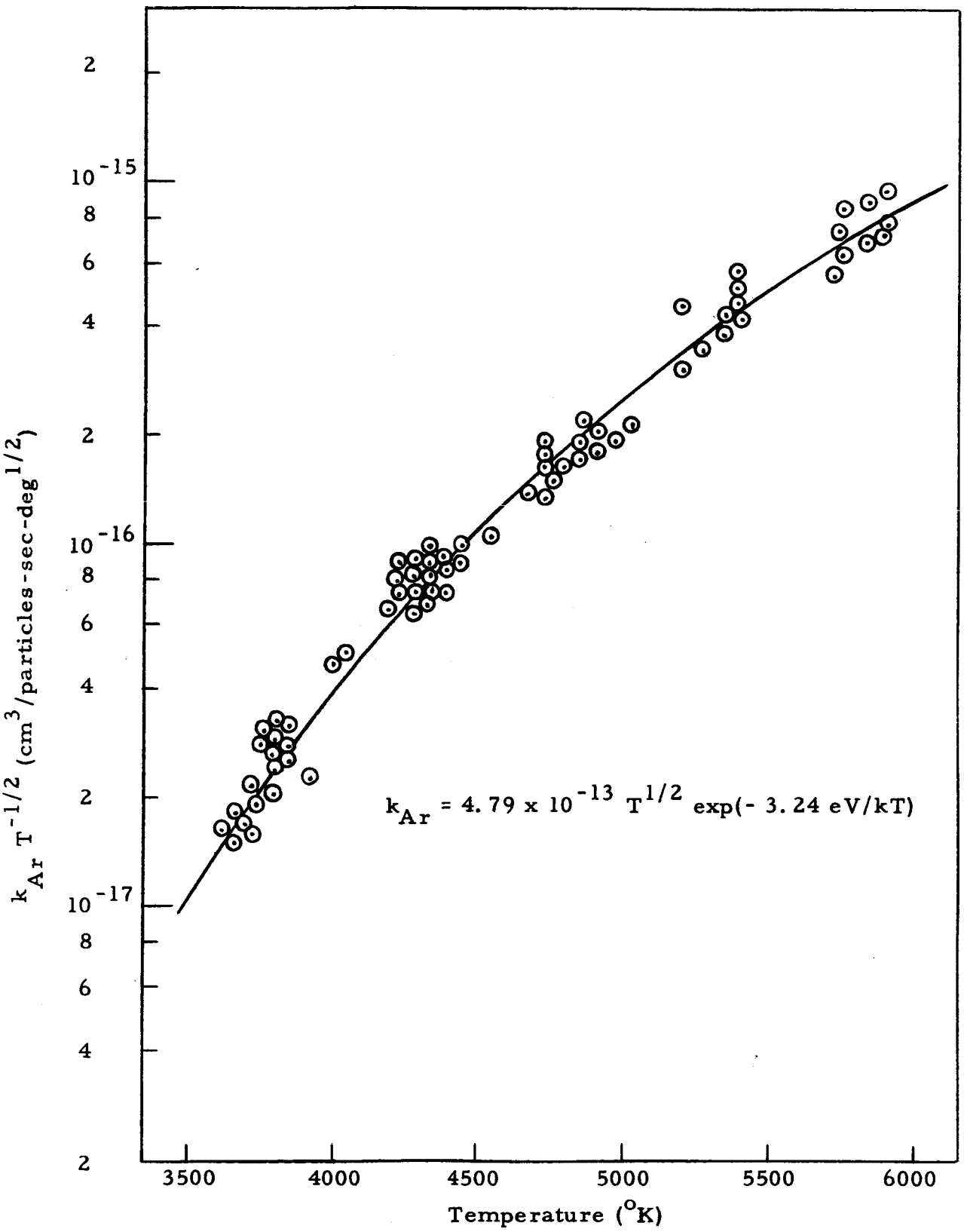


Fig. 3 Arrhenius Plot of CO_2 Dissociation Rate vs. Temperature for One Percent CO_2 in Argon

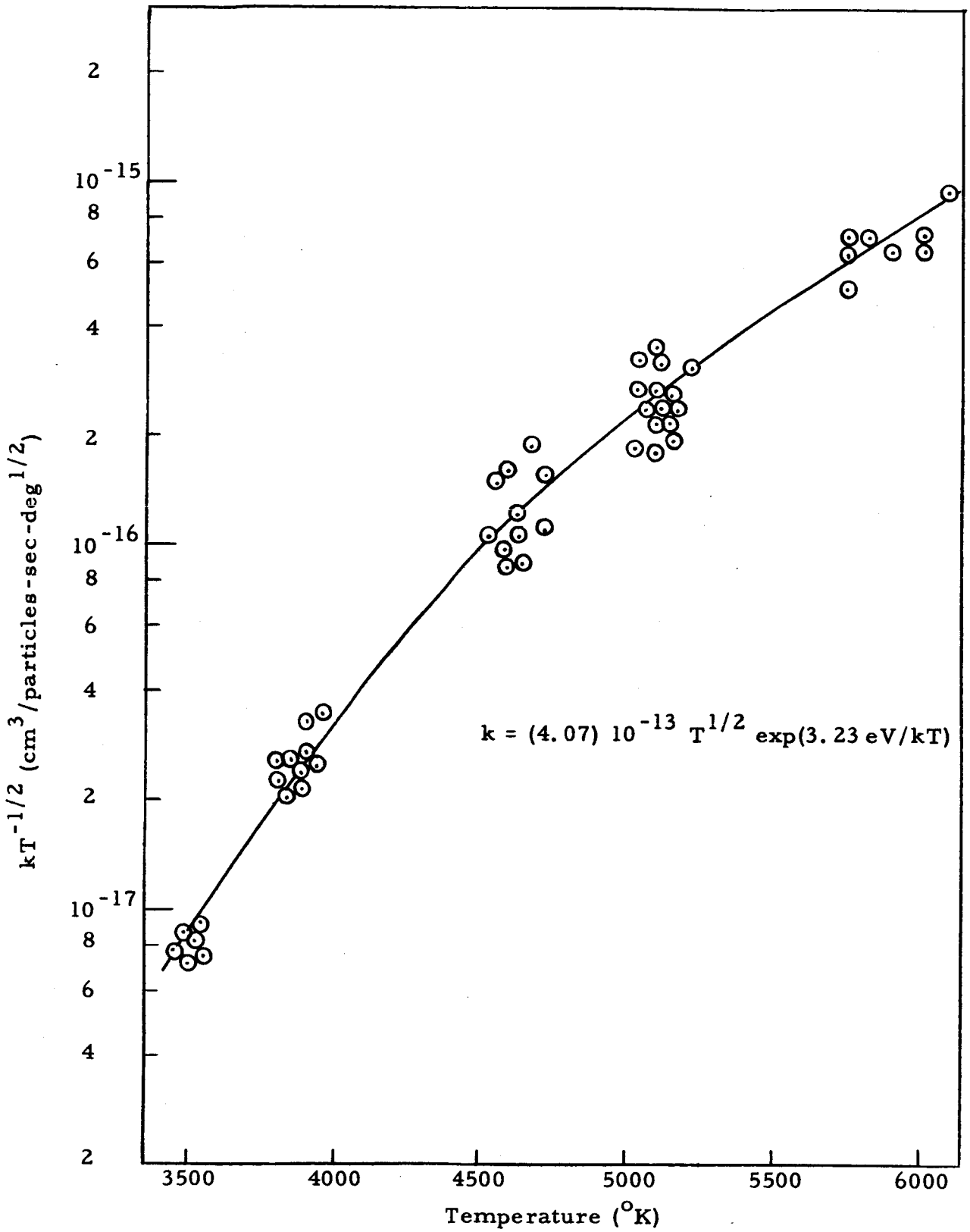


Fig. 4 Arrhenius Plot of CO_2 Dissociation Rate for One Percent CO_2 in Nitrogen

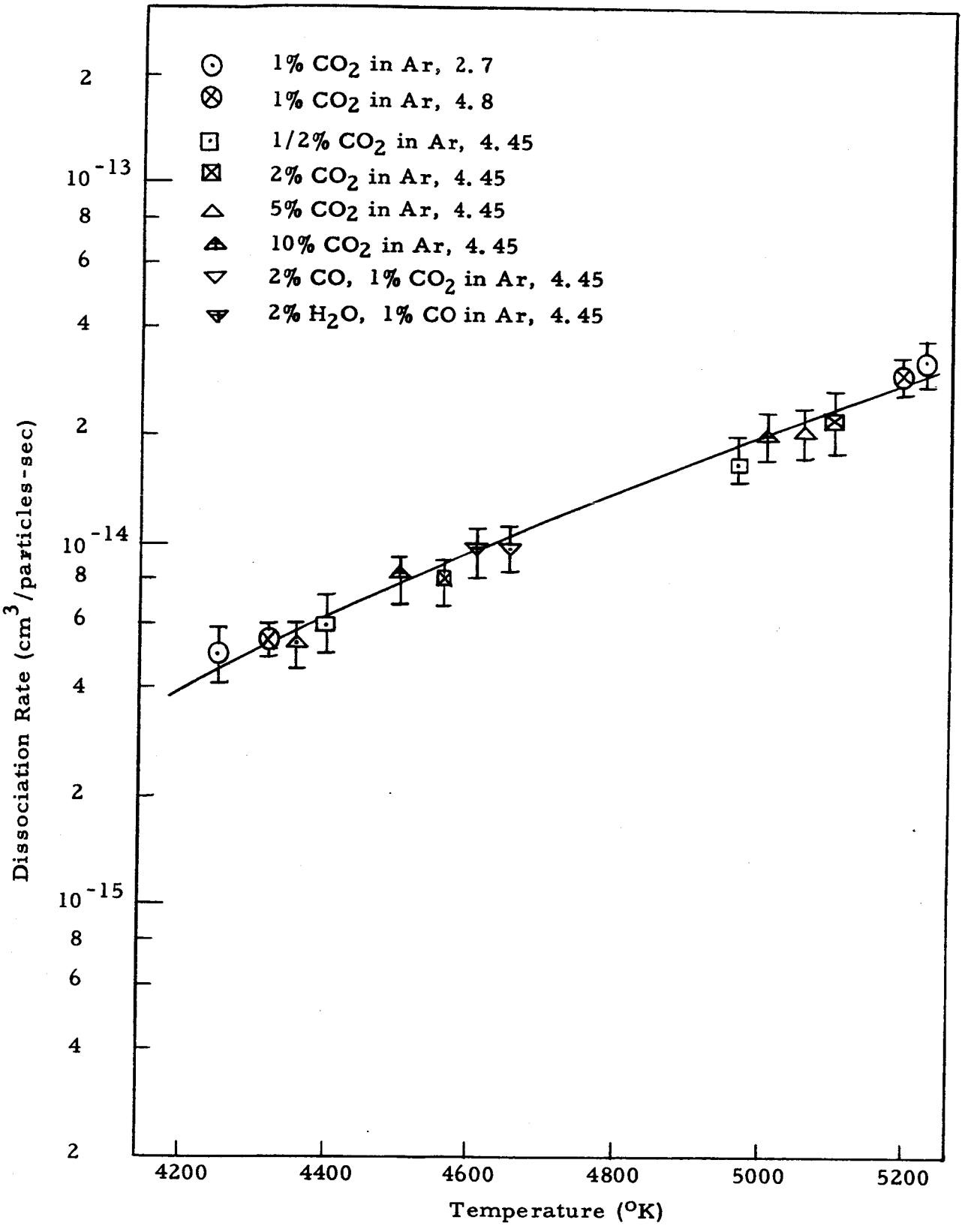


Fig. 5 Dissociation Rate of CO_2 vs Temperature for Variations of Gas Mixture and Wavelength

for argon and nitrogen, respectively, as the collision partners. The activation energies of 3.24 eV for argon and 3.23 eV for nitrogen are considerably less than the CO bond dissociation energy of 5.45 eV required to dissociate ground state CO_2 to ground state products, which indicates that the dissociation involves other than just ground state species. High temperature measurements of dissociation rates generally yield activation energies less than the bond dissociation energy, and this is taken as an indication that dissociation proceeds from excited vibrational levels.[7]

Brabbs et al[5] have measured the dissociation rate of CO_2 behind reflected shock waves in CO_2-Ar mixtures for temperatures from 2500°K to 3000°K. The disappearance of CO_2 was determined by (a) the single pulse technique,[8] in which the gas behind the reflected shock wave is quenched by a rarefaction wave and then chemically analyzed, and (b) measurements of light intensity in the blue continuum due to $CO_2(^3\Pi) \rightarrow CO_2(\Sigma^1) + h\nu$. Their data fit the Arrhenius equation

$$k = 3 \times 10^{11}\ T^{1/2} \exp(-86{,}000/kT)\ cm^3\ mole^{-1}\ sec^{-1} \qquad (10)$$

The dissociation rates calculated with eqn. 6 for temperatures of 2500°K to 3000°K are about twice those obtained with eqn. 10, which is probably good agreement considering the difficulty of both experiments. The dissociation rates calculated with eqn. 10 for temperatures of 4000°K to 6000°K are from three to four times less than those obtained with eqn. 6. The activation energy of 3.74 eV given by Brabbs is higher than the 3.24 eV determined by this experiment, which is consistent with the higher vibrational excitation in the 4000°K to 6000°K temperature range.

REFERENCES

1. W. O. Davies, "Radiative Energy Transfer on Entry into Mars and Venus", ARF Report 1200-1, February 1962.
2. W. O. Davies, "Radiative Energy Transfer on Entry into Mars and Venus", ARF Report 1200-2, June 1962.
3. R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge University Press, New York, 1939.
4. L. S. Kassel, "The Kinetics of Homogeneous Gas Reaction", Chemical Catalog Co. Inc., New York, 1932.
5. T. A. Brabbs, F. E. Belles, and S. A. Zlatarich, J. Chem. Phys. 38, 1939 (1963).
6. S. W. Benson, "Foundations of Chemical Kinetics", McGraw-Hill Book Co., Inc., New York, 1960.
7. H. O. Pritchard, J. Phys. Chem. 65, 504 (1961).
8. H. S. Glick, W. Squire and A. Hertzberg, 5th Symp. Combustion, Pittsburgh, 1954, 393 (1955).
9. W. C. Griffith, Phys. Rev. 102, 1209 (1956).

APPENDIX I

EXPERIMENTAL METHOD AND DATA ANALYSIS

APPENDIX I

EXPERIMENTAL METHOD AND DATA ANALYSIS

The measurements of dissociation rate were made with the shock tube and optical system previously used in the study of CO_2 and CO emissivity[1] (Fig. I. 1). Radiation from behind the shock wave is collimated by slits Sl, and focused on the entrance slit of the infrared monochromator. The infrared radiation emerging from the monochromator is focused on a rapid response InSb detector, whose output signal is amplified, displayed on an oscilloscope, and photographed (Fig. I. 2). When the shock wave passes the slit system there is an initial rapid rise in the infrared emission resulting from the compression and heating of the test gas. Following this rise there is a nearly exponential decay of emission intensity which indicates a decrease in the population of excited vibrational states of $CO_2(X\Sigma^1)$. This decrease is interpreted as CO_2 dissociation.

To obtain the dissociation rate the relation of the emission intensity to the CO_2 concentration must be known. The observed radiation could depend on the gas temperature and pressure, as well as the strength and optical density of CO_2 and any other infrared active gases that are present. Most of the measurements were made with a gas consisting of one percent CO_2 in either argon or nitrogen. The temperatures were calculated on the assumption that the translational, rotational, and vibrational equilibrium were complete before significant dissociation occurred. The nitrogen and argon serve as a heat bath, so that the temperature and pressure just behind the shock wave are not significantly influenced by the chemical reaction.

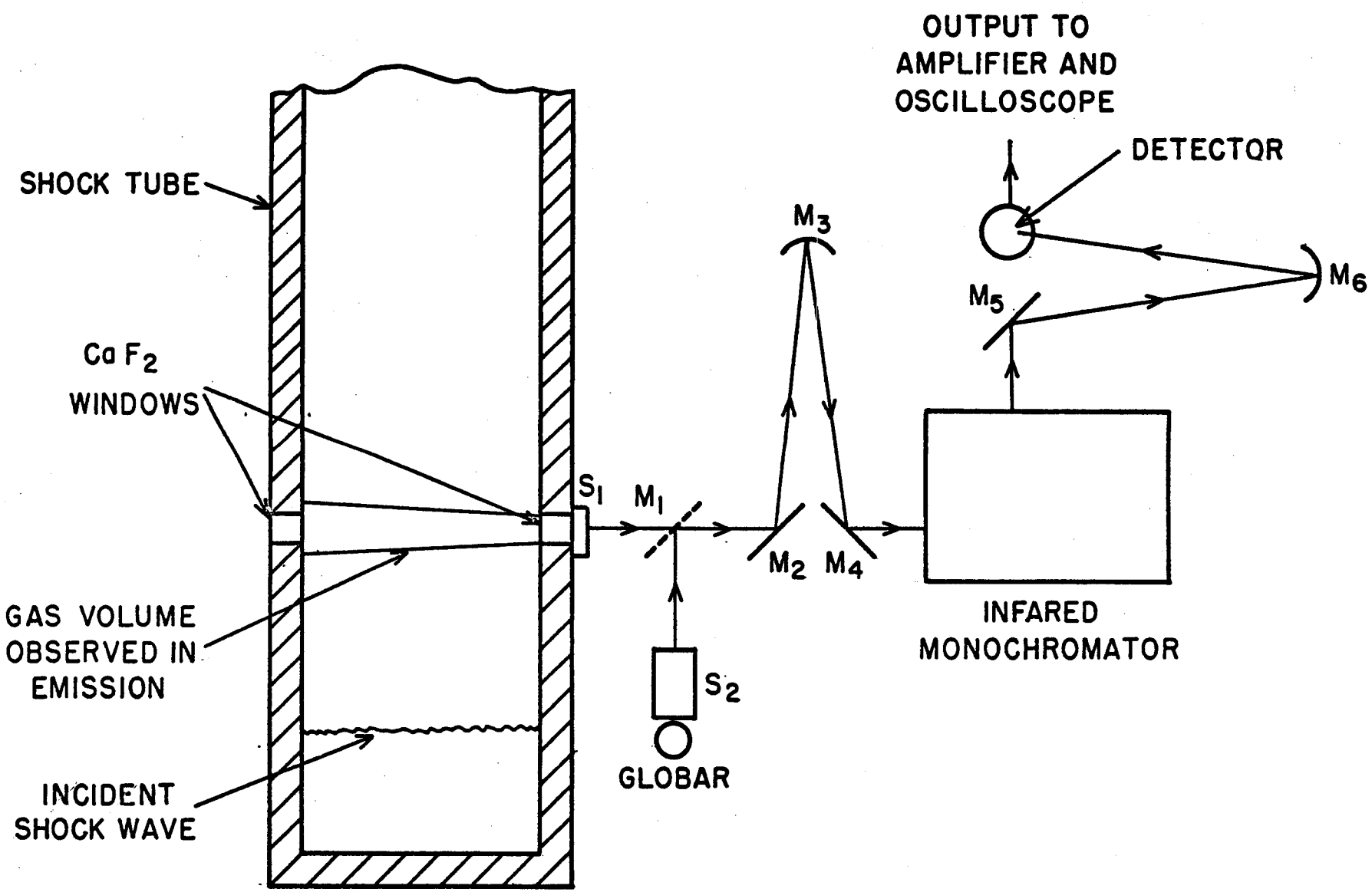
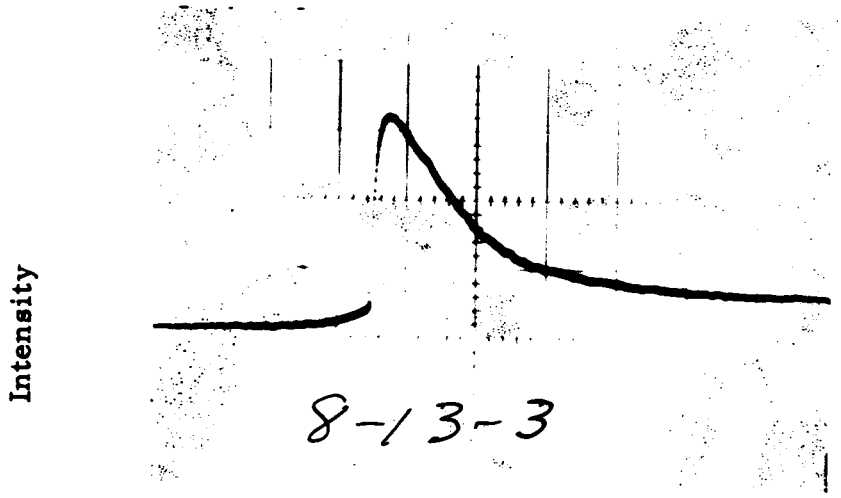


Fig. I. 1 OPTICAL SYSTEM FOR EMISSION MEASUREMENTS



Time (50μs/cm)

Fig. I.2 CO_2 Emission vs. Time.
Gas Mixture - 1% CO_2, 99% Ar. Temperature - 4340°K
Pressure - 0.50 atm. Wavelength - 4.45μ
Time Sweep - 50μs/cm.

It can also be shown that for the pressures used in this experiment, the CO_2 emission is independent of the total pressure. At a temperature of 2000°K the emission is insensitive to pressure above about 0.50 atm (Fig. 32, Ref. 2). This is essentially a statement that the weak line approximation applies, which implies a considerable overlapping of rotational lines. At higher temperatures a larger number of overlapping lines will be excited so that the emission will continue to be insensitive to changes in total gas pressure.

The optical densities for the mixture of one percent CO_2 in either argon or nitrogen were of the order of 0.05 atm-cm. From previous measurements of CO_2 emission it can be seen that for this optical density the observed radiation is linear with optical density for temperatures of 2000°K to 3000°K.[2] As the temperature is increased the band shifts to longer wavelengths, and the emission remains linear with optical density over a larger range of optical densities.

Carbon monoxide is probably the only infrared active dissociation product that would cause an erroneous analysis of the oscilloscope traces. Although the fundamental vibration band of CO (4.67μ) will contribute to emission at 4.45μ, the strength of the CO fundamental band is about ten percent of the CO_2 4.3μ band, and the measurements were made at a wavelength where the ratio of CO_2 to CO emission is even greater.[2] If equal amounts of CO_2 and CO were present the CO emission at this wavelength would be ~ five percent of the CO_2 emission, and this was further reduced by making the measurements just behind the shock wave before appreciable CO formation. The oscilloscope trace (Fig.I.2)does show a measurable emission after equilibrium is reached even for the temperature at which CO_2

dissociation should be complete. That this is infrared emission from CO formed by the dissociation process has been confirmed by observing emission from shock waves in CO-Argon and CO-N_2 gas mixtures, and by varying CO_2 and CO concentrations in CO_2-CO-Argon and CO_2-CO-N_2 mixtures. In general the analysis of the oscilloscope trace includes the effect of CO formation, but for most of the data this correction is negligible.

Although most of the data were obtained with a gas mixture of one percent CO_2 in either argon or nitrogen at a wavelength of 4.45μ, some additional measurements were made to investigate the influence on dissociation rate of (a) the CO_2 concentration, (b) the addition of H_2O or CO to the test gas, and (c) the wavelength at which the measurement is made. The measurements of dissociation rate with one-half, two, five, and ten percent CO_2 in argon are in agreement with those obtained using one percent CO_2 in argon. There are two ways in which the presence of H_2O might affect the results: (a) The vibrational relaxation of CO_2 is more rapid in the presence of water,[7] so that if dissociation proceeds primarily from upper vibrational states then the dissociation rate might be affected. (b) H_2O is infrared active and has a dissociation energy of 4.7 eV, so shock heated water might produce a decaying infrared signal similar to that of CO_2. It was determined that the emission from a mixture of two percent water in argon is not significant at the wavelength and instrument sensitivities used for the dissociation measurements. The dissociation rate was determined with gas mixtures of one percent CO_2 in argon containing both H_2O or CO concentrations from one-half to two percent. These results indicate that the presence of up to two percent water does not effect the reaction rate, and the addition of CO increases the level of equilibrium

emission but does not influence the rate constant.

The dissociation rate for one percent CO_2 in argon was also determined at wavelengths of 4.80 μ and 2.70 μ, and for pass bands from 0.02 μ to 0.08 μ at the principal measuring wavelength of 4.45 μ. At 4.8 μ the emission is also from the 4.3 μ CO_2 band, but in a region where the emission is much weaker and the CO emission is relatively stronger. The measurement at 2.7 μ involves the emission from the two combination bands of CO_2 arising from the transitions $(n_1+1, n_2^{\ell}, n_3+1 \rightarrow n_1, n_2^{\ell}, n_3)$ and $(n_1, n_2+2^{\ell}, n_3+1 \rightarrow n_1, n_2^{\ell}, n_3)$. None of these variations alter the rate constant within the experimental error.

The measurements were analyzed on the assumption that the dissociation process being observed is $CO_2 \rightarrow CO + O$. The observations were made just behind the shock wave in a region far from equilibrium so that the reverse reaction could be neglected. The rate of disappearance of CO_2 is described by the first order reaction

$$d(CO_2)/dt = - k_M(CO_2)(M) \qquad \text{(I. 1)}$$

where (M) refers to the concentration of either argon or nitrogen, and it is assumed that the terms containing products of CO_2 and other atom or molecule concentrations are negligible because of the low concentration of CO_2 and other species. The concentration of CO_2 is given by

$$(CO_2) = (CO_2)_o \exp\left(- k_M(M)t\right) \qquad \text{(I. 2)}$$

and the dissociation rate constant is

$$k = \ln 2/(M)t_{1/2} \qquad \text{(I. 3)}$$

where $t_{1/2}$ is the half-life obtained from the oscilloscope trace. The variation of emission intensity with time is exponential, so the half-life can be obtained from a plot of the logarithm of intensity vs. time.

The rate constants were fit by the method of least squares to the classical collision theory for diatomic molecules to provide an analytical expression that describes the rate constant as a function of temperature. Only collisions of the carrier gas, i.e. the argon or nitrogen, with CO_2 were considered, and the result of this collision was assumed to be the production of CO molecules and O atoms. According to the classical collision theory[3] the rate of change of CO_2 concentration is

$$d(CO_2)/dt = ZP\ (D/kT)^S/S!)\ \exp\ (-\ D/kT) = k_M(CO_2)(M) \qquad \text{(I. 4)}$$

where Z is the collision frequency, the steric factor P is the probability that a collision with sufficient energy will produce dissociation, D is the dissociation energy, k is the Boltzmann constant, T is absolute temperature, and S is a factor that accounts for the number of transverse translational and internal energy degrees of freedom that contribute energy to the dissociation process. The collision frequency is

$$Z = (CO_2)(M)(\pi r^2)\ (8\ kT/\pi m)^{1/2} \qquad \text{(I. 5)}$$

where r is the effective collision radius and m is the reduced mass of the CO_2-M system, and the rate constant becomes

$$k = (P\, r^2/S!)(8\pi kT/m)^{1/2}\ (D/kT)^S\ \exp(-D/kT) \qquad \text{(I. 6)}$$

Since the choice of the steric factor P, the collision radius r, and the value of S are uncertain, the rate constants were fit by the method of least squares to the equation

$$k = C\ (D/kT)^n \exp(-D/kT) \qquad \text{(I. 7)}$$

to provide the constants C and n, which are used to determine S and P.

There are a number of assumptions inherent in the attempt to describe this reaction with the classical collision theory. The expression for the rate constant is derived for collisions involving a diatomic molecule, so that in this application the CO and O take the place of the two atoms. This appears to be a reasonable assumption for the temperatures 3500°K to 6000°K that were considered. At equilibrium conditions for these temperatures there would be very little CO_2 and O_2, so that in the region just behind the shock wave the system is far from equilibrium, and the reactions $O + O \rightarrow O_2$ and $CO + O \rightarrow CO_2$ would be slow. Thus the main products of the reaction in this region are CO molecules and O atoms. Even at the highest temperatures considered the degree of CO dissociation is essentially zero and that of N_2 is ~ five percent, so that transient species such as CN and NO will not be formed in sufficient quantities to disturb the measurement.

The factor S in the expression for the rate constant is a measure of the degrees of freedom, other than translation along the line of centers, that contribute energy to the dissociation process. The maximum value for S can be calculated by considering the number of atoms and degrees of freedom involved in the collision. For a CO_2-Ar collision, the maximum value is six if rotation is included, and five if it is not; for CO_2-N_2 collisions the corresponding numbers are eight and six.

The dissociation rate data were also analyzed by a least squares fit to the Arrhenius equation of the form

$$k = C\,T^{1/2} \exp(-\,Q/kT) \qquad \text{(I. 8)}$$

in which the values of C and the activation energy Q are determined empirically. It is expected that the apparent activation energy will be less than the CO band dissociation energy, because dissociation will occur from excited vibrational levels.