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A SURVEY OF VIBRATIONAL RELAXATION
RATE DATA FOR PROCESSES IMPORTANT TO
CO₂-N₂-H₂O INFRARED PLUME RADIATION

Jay A. Blauer, et al

Ultrasystems, Incorporated

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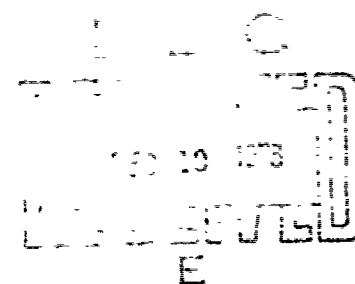
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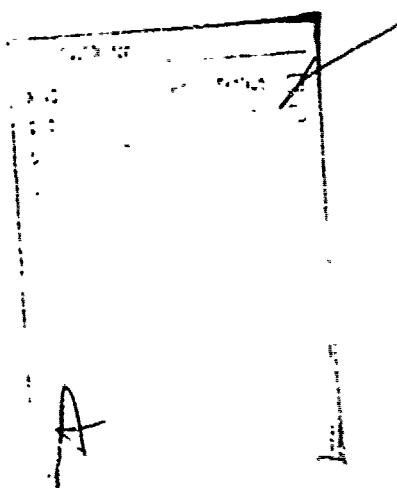
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13. ABSTRACT A comprehensive survey of relaxation rate data important in the modeling of non-equilibrium infrared radiation from exhaust plumes at altitude is presented. A model is developed which considers energy transfer among the first fourteen vibrational states of CO ₂ , the first five of H ₂ O, and up to the first three states of each of the diatomic molecules considered, i.e., of N ₂ , O ₂ , CO, OH, and H ₂ . Available data are first assembled for those processes that have been subjected to experimental analysis. Where possible, statistical and/or quantum considerations are used to relate unmeasured rate constants to those whose values are known. Finally, resort is made to available theory to obtain estimates for the rate constants for the balance of the interactions important to the overall model.			

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FOREWORD

This technical report is submitted by Ultrasystems, Inc. in accordance with the provisions of Air Force Contract F04611-73-C-0032 entitled "Non-Equilibrium Radiation Model for Exhaust Plumes" and has been assigned Ultrasystems Report Number SN-8225/TR. The report was prepared for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California.

The purpose of this report is to summarize all important V-V and T-V relaxation rate information that has been collected under Phase I of this contract. This report can be considered as a part of the final report required for the subject contract. A comprehensive literature survey of the subject matter has been conducted, and, in addition, theoretical methods have been used to estimate relaxation rates for those processes for which no experimental data could be found. The results contained in this report should prove useful to those currently modeling the chemical kinetics of either exhaust plumes or lasers that involve the molecules studied.

Work presented in this report began in November 1972 and concluded in May 1973. The program was conducted within the Engineering Sciences Department of Ultrasystems Inc. at their Irvine facility. This report was co-authored by Dr. Jay A. Blauer and Mr. Gary R. Nickerson. The Air Force Program Monitor was Lt. Peter C. Sukanek (AFRPL/DYSP).

This technical report has been reviewed and is approved.

Paul J. Daily
Colonel, USAF
Chief, Technology Division

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NOMENCLATURE

$\langle f \rangle$	molecular orientation averaging function.
k	bimolecular rate constant in units of cc/mole-sec.
l	quantum number for vibrationally induced rotational motion in CO_2 . also used as the range parameter of the repulsive potential function.
m	reduced mass of the collision pair.
M_i	the atomic weight of the i^{th} particle of a molecule.
M_s	effective molecular weight for the s^{th} vibrational mode.
$\bar{M}$	reduced molecular weight of the collision pair.
P	transition probability
q	the matrix element of the oscillator's internal coordinate.
Q	the quadrupole moment.
s	step number index of SSH theory
S	a statistical factor which accounts for the degeneracy of an energy transfer process.
T	absolute temperature in degrees Kelvin.
v	vibrational quantum number
Z	average number of collisions required to cause a vibrational transition.
Z_{AB}	bimolecular collision frequency.
Z_{tr}	the contribution of relative translational motion to the value of Z as described in the SSH theory.
Z_o	a steric factor appearing in SSH theory.
$(Z_s)_{osc}$	the contribution of vibrational motion from step s of an overall process to the value of Z as described in the SSH theory.
α	energy contribution of dipole-dipole attraction.
α_s^2	a function relating Cartesian and normal vibrational coordinate.
β	energy contribution of dipole-quadrupole attraction.
ΔH	enthalpy difference between an excited state and the ground state
Δl	change in the value of the quantum number, l .
Δv	change in a vibrational quantum number, v
$\Delta 6$	vibrational energy converted to translational motion in an overall energy exchange process.

ϵ/k	the Lennard-Jones attractive potential.
θ	the characteristic vibrational temperature of a molecule
μ	the dipole moment.
σ	Lennard-Jones collision diameter
X_1	transition moment.
Ψ	vibrational wave function.
ω_s	the change in vibrational frequency during the s^{th} step.

1. INTRODUCTION

Theoretical performance predictions of any combustion process depend not only upon assumptions regarding the species present but also upon the nature of the reactions taking place. In rocket propulsion problems, the simplifying assumption of thermodynamic equilibrium is usually made. However, for some engines performing at altitude, there is convincing experimental and analytical evidence that nonequilibrium conditions exist in both the nozzle and the freely expanding plume. Accordingly, an accurate mathematical description of plume radiation must consider the kinetic events that permit non-equilibrium conditions to exist in the flowfield.

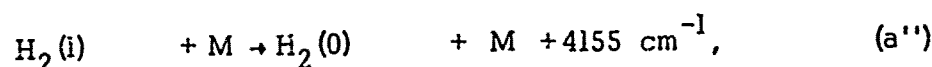
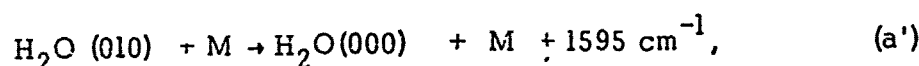
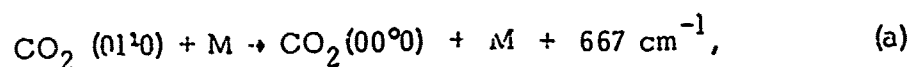
In order to obtain useful estimates of the infrared radiation from plumes at altitude, it becomes necessary to know the rates of vibrational energy transfer among the molecules that make up the plume flowfield. Although considerable information is available at the present time¹⁻⁶⁰ regarding energy transfer between the major molecular species that make up typical plume environments (i.e. CO_2 , CO , N_2 , H_2O , H_2), considerable reliance must also be made upon theoretical estimates for the rates of processes that have not been subjected to experimental investigation. Fortunately, it is frequently possible by statistical or quantum considerations to find relationships between known and unknown rate constants. In those cases for which this is not possible, recourse must be made directly to available theory.

The problem under consideration has obvious parallels to those encountered in the mathematical description of the gas dynamic laser. As such, we are able to rely heavily upon the earlier review given by Taylor and Bitterman concerning rates of importance to the CO_2 - N_2 laser system¹.

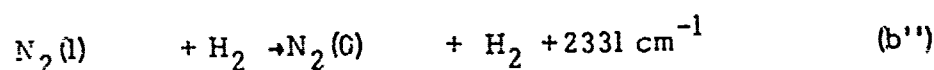
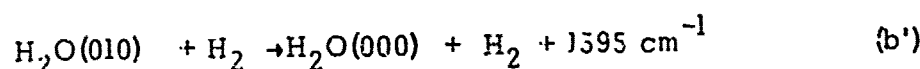
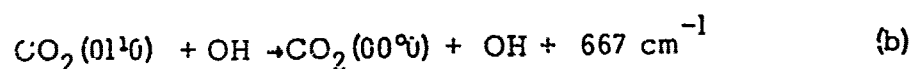
2. MECHANISM.

Vibrational energy transfers may be classified into at least three distinctive categories: Vibration-to-Translation (V-T), Vibration-to-Rotation-to-Translation (V-R-T), and Vibration-to-Vibration (V-V). In addition, there are two subgroupings of V-V processes depending upon whether the transfer is intermolecular or intramolecular. Examples of each of these processes are to be found in the following listing:

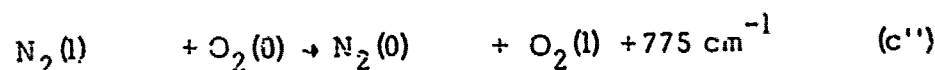
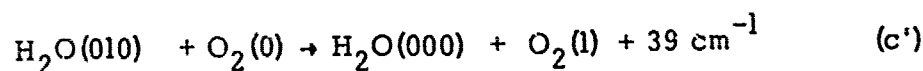
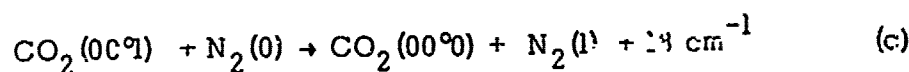
V-T Processes



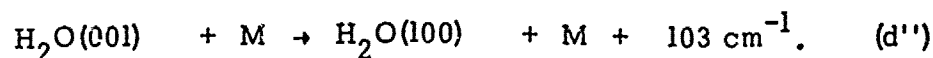
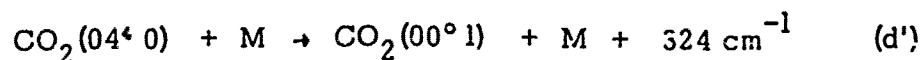
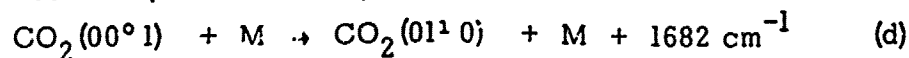
V-R-T Processes



V-V Processes (intermolecular)



V-V Processes (Intramolecular)



It has been suggested that in molecules with small moments of inertia (e.g. OH, H₂O, etc.) vibrational energy may be first transferred into the rotational degrees of freedom rather than directly into translation^{41,56,67}. Convincing evidence has been presented which suggest that in collisions with hydride like species, polyatomic molecules such as CO₂ and H₂O are deactivated in this manner⁷⁰. Accordingly, although the energy requirements for V-T and V-R-T energy transfers are the same, a distinction has been made here between these processes and they are subsequently treated by different theoretical methods.

Before proceeding further it is appropriate to briefly review nomenclature and the selection rules for vibrational transitions in CO₂, H₂O, and the diatomic molecules.

Carbon dioxide is a linear triatomic molecule, and as such it has three normal vibrational frequencies, one of which is degenerate. In addition, by virtue of its linear nature, it has a vibrational rotation mode about its inter-nuclear axis. Accordingly, four quantum numbers are required to completely specify its vibrational state³⁹. A typical spectroscopic symbol for this molecule will have the form CO₂(mn^lp). The integers m, n, and p specify the values of the three vibrational quantum numbers ν_1 , ν_2 , and ν_3 ; whereas, the integer l will be even or odd depending upon whether ν_2 is even or odd; furthermore, the following relationship holds:

$$l = \nu_2, \nu_2 - 2, \nu_2 - 4, \dots, 1 \text{ or } 0.$$

During a radiative transition involving the CO_2 molecule, the following selection rules describe the processes which are possible⁴⁶.

$$\begin{aligned}\Delta v_1 &= \pm 1, 0, \\ \Delta v_2 &= \pm 1, 0, \\ \Delta v_3 &= \pm 1, 0, \\ \Delta l &= \pm 1 \text{ whenever } \Delta v_2 = \pm 1, \\ \Delta l &= 0 \text{ whenever } \Delta v_2 = 0.\end{aligned}$$

These rules have a quantum mechanical origin and are based upon an assumption that the molecular motions involved are simple harmonic. Herzfeld and his co-workers⁶¹ have treated the collision induced transfer of vibrational energy from a quantum mechanical standpoint. The basic assumption underlying their treatment is that the minimum displacement X of the oscillator nuclei from their equilibrium separation r_e during a collision is small compared to the instantaneous distance x between the incident atom and the center of mass of the oscillators. They expand the interaction energy $U(x-X)$ as a power series in X about r_e and neglect all terms of order X^2 or higher. In this approximation, for harmonic oscillators, the above simple selection rules are shown to apply. More recently, Shuler and Zwanzig⁴² have shown that for harmonic oscillators undergoing impulsive hard sphere collisions of high energy, the simple selection rules break down and multiquantum transitions become possible. Treanor et al⁹³ have treated the problem on the basis of an anharmonic oscillator and find marked departure from the model described here under conditions of high vibrational energy coupled with low translational temperature. The net effect is to increase the rate of relaxation when the vibrational energy is high, i.e. under conditions prevailing when the energy inversion is large. Accordingly, as the temperature at which the vibrationally excited species are produced is increased we will expect increasing departure from the simple rules given above. Nevertheless, in line with the assumptions of Herzfeld and other^{1,15,22,61} and for the sake of brevity, we will assume that the rules do apply.

Due to an accidental degeneracy between the modes v_1 and $2v_2$ in CO_2 there is a mixing of the wave functions (linear combination) to form two new states that are assumed to be in local equilibrium (Fermi resonance)³⁹. This equivalence of states is designated by placing both sets of symbols within the parenthesis. Actually, there are two states of slightly different energy that will then have the same spectroscopic symbols. They are differentiated, by primes. We have for example the states $(02^\circ 0, 10^\circ 0)'$ and $(02^\circ 0, 10^\circ 0)''$ at 1285 cm^{-1} and 1388 cm^{-1} above the ground state. In the present survey, only the total rate of energy flow into or out of both states is considered. Any attempt to consider all of the states in Fermi resonance individually would make the problem intractable at the present time.

The vibrational state of water requires only three quantum numbers. Accordingly, the symbol $\text{H}_2\text{O}(mnp)$ designates that the integer values of the three quantum numbers v_1 , v_2 , and v_3 are m , n , and p respectively. The selection rules that are assumed to apply for vibrational exchanges involving this molecule are as follows:

$$\begin{aligned}\Delta v_1 &= \pm 1, 0 \\ \Delta v_2 &= \pm 1, 0 \\ \Delta v_3 &= \pm 1, 0\end{aligned}$$

The vibrational state of a diatomic molecule requires only one quantum number for complete specification. Accordingly, the symbol $\text{N}_2(n)$ specifies that there are n quanta of vibrational energy in the N_2 molecule. The selection rule holding in these cases is assumed to be as follows:

$$\Delta v = \pm 1$$

Although a very large number of rates must be known for a complete specification of the vibrational energy transfer in a plume flowfield, not all routes for energy transfer are equally efficient. Accordingly, a very satisfactory description of nonequilibrium radiation can be obtained from a knowledge of a limited number of important rates. It is the intent of this compilation to not only provide rate data but also offer some guidance regarding their relative importance.

3. THEORETICAL MODELS AND STATISTICAL INTER-RELATIONSHIPS

Hertzfeld²² has adapted the well-known SSH theory to the specific case of vibrational energy transfer in CO_2 in the presence of Fermi resonance. The overall relaxation equation is written in an abbreviated form, i.e.,

$$Z = 1.017 \left(\frac{Z_0}{S} \right) Y Z_{\text{tr}} \exp \left(- \frac{\epsilon}{kT} - \frac{\Delta\theta}{2T} \right) \prod_s (Z_s)_{\text{osc}} \quad (1)$$

The quantity Z is the average number of collisions required to cause a vibrational transition to occur; Z_0 is a steric factor to be discussed later; Z_{tr} is the contribution of relative translational motion to Z ; and then $(Z_s)_{\text{osc}}$ represents the contribution of vibrational motion from steps in the overall process. These and other quantities are defined further below. It is to be noted that in multistep processes, the value for Z_{tr} is computed for the overall process, whereas, each step contributes its individual value for $(Z_s)_{\text{osc}}$. In equation (1)

$$Y = 0.76 \left(1 + 1.1 \frac{\epsilon}{kT} \right)$$

$$Z_{\text{tr}} = \pi^2 \left(\frac{3}{2\pi} \right)^{1/2} \frac{(\Delta\theta)^2}{\theta'} \left(\frac{T}{\theta'} \right)^{7/6} \exp \left[\frac{3}{2} \left(\frac{\theta'}{T} \right)^{1/2} \right]$$

The energy exchanged between vibrational and translational degrees of freedom ($\Delta\theta$) refers to the overall process regardless of the number of steps.

$$\theta' = 0.8153 \tilde{M} \ell^2 (\Delta\theta)^2$$

$$(Z_s)_{\text{osc}} = 0.0413 \sigma_s^2 M_s \ell^2 \theta_s$$

One value for $(Z_s)_{\text{osc}}$ for each step (s) in the overall process appears in the expression for Z . This Z value is strictly for a single transition, i.e., the factor $(1 - e^{-\theta/T})$ is omitted*.

*In this study, the factor $(1 - e^{-\theta/T})$ has been used only to relate deactivation rates to the experimentally observed overall deactivation rates of specific vibrational modes.

$$\theta_s = hc \omega_s / k,$$

Z_o = steric factor,

s = step no. index,

S = a statistical factor that accounts for the degeneracy of the energy transfer process,

$\bar{M}$ = reduced molecular weight of collision pair,

ϵ/λ = Lennard-Jones attractive potential,

α_s = a function whose derivation depends upon the relationship between the cartesian vibrational coordinates of the molecule and the corresponding normal coordinates,

ω_s = the change in vibrational frequency during the s^{th} step,

$\Delta \theta$ = vibrational energy converted to transitional motion in the overall process,

M_s = the effective molecular weight for the vibrational mode involved in the s^{th} step of the overall transition,

ℓ = the range parameter of the repulsive potential function.

The function α_s^2 has the following form for a CO_2 molecule, the numbers 1,2,3 being applied to the atoms OCO, respectively:

$$\alpha_1^2 = \frac{1}{4},$$

$$\alpha_2^2 = \frac{4 M_1^2 + M_2^2}{2 (2 M_1 + M_2)^2},$$

$$\alpha_3^2 = \left(\frac{M_2}{2 M_1 + M_2} \right)^2.$$

Furthermore, for CO_2 ,

$$M_s = M_1/2 \text{ for } s=1,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} \text{ for } s=2,3.$$

For H_2O the function α_s^2 has the following form, the numbers 1,2,3 being applied to the atoms HOH, respectively:

$$\alpha_1^2 = \frac{1}{4+2M_1(\cos \theta)^2} \cdot \frac{M_2}{M_2}$$

$$\alpha_3^2 = \frac{\left(\frac{2M_1M_2}{2M_1+M_2}\right) \frac{2M_1M_2^2}{(2M_1+M_2)^2 \tan^2 \theta}}{2M_1+M_2 \left[\frac{2M_1}{M_2} \sin \theta\right]^2} \cdot$$

The value for α_2^2 is not needed in our argument and will not be given here. Furthermore, for H_2O ,

$$M_s = M_1/2 \text{ for } s=1,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} \text{ for } s=2,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} + \frac{2M_1M_2^2}{(2M_1+M_2)^2 \tan^2 \theta} \text{ for } s=3,$$

where θ is the half angle of the isosceles triangle, formed by the two H-O bonds in the water molecule.

For a diatomic molecule,

$$\alpha_s^2 = \frac{M_1^2 + M_2^2}{2(M_1 + M_2)^2}$$

$$M_s = \frac{M_1 M_2}{M_1 + M_2}$$

The range parameter ℓ was evaluated by means of method B of reference 61 and involves an iterative solution of the following two equations:

$$\frac{\epsilon_m}{k} = .5949 \left[\tilde{M} (\omega \ell T)^2 \right]^{1/3}$$

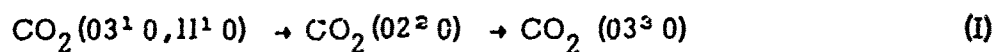
and

$$\sigma/\ell = \left\{ \ln \left(\frac{\epsilon_m}{\epsilon} + 1 \right) \left[1 - \left(\frac{1 + \sqrt{\frac{\epsilon_m}{\epsilon} + 1}}{2} \right) \right]^{-1/6} \right\}$$

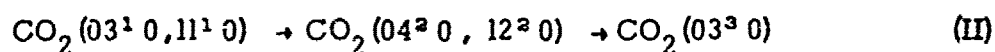
As an example of the approach followed in this review for the evaluation of the statistical factor ζ , we consider the following transfer of energy:



Due to the selection rules, this process is treated in a two-step manner for which there are two equivalent paths of lowest energy, i.e.,



and



In accordance with the procedure outlined by Herzfeld²², we express the wave functions for the three states involved in the second path in the following manner:

$$\Psi(03^1 0, 11^1 0)' = a' \Psi_1(0) \Psi_2(3^1) + b' \Psi_1(1) \Psi_2(1^1)$$

$$\Psi(03^1 0, 11^1 0)'' = a'' \Psi_1(0) \Psi_2(3^1) + b'' \Psi_1(1) \Psi_2(1^1)$$

$$\Psi(04^2 0, 12^2 0)' = f' \Psi_1(0) \Psi_2(4^2) + g' \Psi_1(1) \Psi_2(2^2)$$

$$\Psi(04^2 0, 12^2 0)'' = f'' \Psi_1(0) \Psi_2(4^2) + g'' \Psi_1(1) \Psi_2(2^2)$$

$$\Psi(03^3 0) = \Psi_1(0) \Psi_2(3^3)$$

As before, the prime and double signatures designate states in Fermi resonance. Beginning with the singly primed states, the transition moment for this path is

$$\begin{aligned} X(\text{II}) &= \int \Psi(03^1 0, 11^1 0) \frac{z_2}{l} \Psi(04^2 0, 12^2 0) dz_1 dz_2 \\ &\quad * \int \Psi(04^2 0, 12^2 0) \frac{z_2}{l} \Psi(03^3 0) dz_1 dz_2 \\ &= \left[a' f' \int \Psi_1(0) \Psi_1(0) dz_1 \int \Psi_2(3^1) \frac{z_2}{l} \Psi_2(4^2) dz_2 \right. \\ &\quad \left. + b' g' \int \Psi_1(1) \Psi_1(1) dz_1 \int \Psi_2(1^1) \frac{z_2}{l} \Psi_2(2^2) dz_2 \right] \\ &\quad \times f' \int \Psi_1(0) \Psi_1(0) dz_1 \int \Psi_2(4^2) \frac{z_2}{l} \Psi_2(3^3) dz_2 . \end{aligned}$$

All other terms are zero due to the orthogonal nature of the wave functions. In terms of the transition moment X_2 with

$$X_2 = \int \Psi_2(1^1) \frac{z_2}{l} \Psi_2(0^0) dz_2$$

the overall transition moment for the second path becomes

$$X(\text{II}) = (a' f' \sqrt{4} + b' g' \sqrt{2}) f' \sqrt{4} X_2^2 = [4a' (f')^2 + \sqrt{8} b' (g' f')] X_2^2$$

After adding to the above the contributions which arise from the doubly primed middle term, we obtain

$$X(\text{II}) = \left[4a' \left[(f')^2 + (f'')^2 \right] + \sqrt{8} b' (g'f' + g''f'')^2 \right] X_2^2$$

The orthogonality condition requires that the term in square brackets be unity; whereas, the term in parenthesis is zero. Accordingly,

$$X(\text{II}) = 4a' X_2^2$$

Since the deactivation probability and hence Z^{-1} are proportional to X^2 , we have

$$X^2(\text{II}) = 16 (a')^2 X_2^4$$

Herzfeld²² leaves the problem at this point to allow for considerations of states in Fermi resonance individually. Since it is our intention to treat only the total energy flux into or out of both states, we add to $X^2(\text{II})$ the contribution due to the doubly primed initial state. Then, due to the orthogonality condition, we have for path II

$$X^2(\text{II}) = 16 X_2^4.$$

Similar considerations for path I give

$$X^2(\text{I}) = 9X_2^4$$

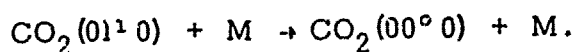
Accordingly, for the sum of both paths we obtain

$$M^2 = 25 X_2^4$$

and the statistical factor, S , for the process is 25. In accord to the treatment outlined here, the statistical factor is simply a function which accounts for the

degeneracies of the reaction paths involved in a given process. The values derived herein for S are of course only as good as the model for which they apply, i.e., that of the harmonic oscillator. Values for Z_0 were obtained in the manner outlined by Herzfeld²².

The approach outlined here is very useful in obtaining statistical inter-relationships between the rates of various processes. Thus, it is possible to statistically relate the rate of any process in CO_2 for which $v_2 = \pm 1$ and $j = \pm 1$ to the experimentally determined rate of the following process:



A large number of rates treated in this review were obtained in this manner.

Although the SSH theory has proven very successful in the estimation of rates of vibrational relaxation for nonpolar molecules, for highly polar molecules of the type typified by H_2O it has been singularly unsuccessful. This is due at least in part to neglect of the attractive portion of the potential function which can be sizeable for molecules of this type. Shin³⁷ has specifically treated the case of H_2O self relaxation in a simple and entirely classical manner. His expression for the collisional transition probability with an assumption of T-V exchange is as follows:

$$P_{10} = \sqrt{\frac{4\pi}{3}} \left(\frac{4\pi m a \Delta}{\pi^2} \right) q^2 \left(\frac{\chi}{kT} \right)^{3/2} \langle f \rangle \exp \left[-\frac{3\chi}{kT} + \frac{4\sqrt{D}\chi}{\pi kT} + \frac{16D}{3\pi^2 kT} + \frac{\Delta}{2kT} \right]. \quad (2)$$

The following definitions apply to equation (2):

m = reduced mass of the collision pair,

$$a = \left[\frac{\Gamma(7/12)}{\Gamma(1/12)} \right] \left(\frac{4D}{\chi} \right)^{1/12} \frac{\sigma}{\sqrt{\pi}},$$

σ = the collision diameter,

$D/k = \epsilon/k$ = Lennard-Jones parameter,

$$\chi = \left[\sqrt{m/2} \pi \Delta a k T / \hbar \right]^{2/3},$$

Δ = change in vibrational energy due to the transition,

$$\langle f \rangle = \frac{\exp(2\alpha)}{16(\alpha^2 - \beta^2)},$$

q = the matrix element of the oscillator's internal coordinate,

$$\alpha = 4464 \left(\frac{\mu^2}{D \sigma^3} \right) \frac{D^{3/4} \chi^{1/4}}{k T},$$

$$\beta = 2815 \left(\frac{\mu Q}{D \sigma^4} \right) \frac{D^{2/3} \chi^{1/3}}{k T},$$

μ = the dipole moment of H_2O ,

Q = the quadrapole moment of H_2O .

For the case of H_2O relaxation by a nonpolar molecule such as N_2 , the value of $\langle f \rangle$ is near unity making the calculation very simple.

Finally, Shin has also considered V-R-T exchanges in a classical manner for several specific cases^{56,62}. For the case of the self relaxation of a hydride his equations take the form

$$P_{10} = Q' f_{vt} \sqrt{\frac{4\pi X}{kT}} \exp \left[-\frac{3X}{kT} + \frac{8\sqrt{gDX}}{kT} + \frac{64gD}{3\pi^2 kT} + \frac{A}{2kT} \right] \quad (3)$$

Where Q' , f_{vt} , and g are rather complicated functions of the input parameters described above, the values of which are liberally discussed in reference 55.

For this review, we have chosen to express results in terms of a kinetic rate constant k which has units of cubic centimeters per mole per second where

$$k(V-T) = \frac{1}{Z_{AB} P(V-T)}$$

and

$$k(V-V) = \frac{1}{Z_{AB} P(V-V)}$$

where Z_{AB} is the bimolecular collision frequency, θ is the characteristic vibrational temperature of the molecule, and the expressions $P(V-T)$ and $P(V-V)$ refer to the collisional transitional probabilities for V-T and V-V processes respectively.

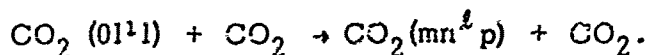
Admittedly, our expression for the rate of a V-T process depends upon an assumption of the harmonic oscillator approximation. While we recognize that, under conditions prevailing when large populations inversions are involved, departures from the model will become noticeable^{42,93}, we have chosen to maintain the approximation in accord with other authors^{1,15,22,61}.

Although there are other theories (e.g., those of Sharma^{63,64}) which may be more satisfying than those of Shin from a quantum mechanical standpoint, the latter were chosen primarily for their ease of utility which apparently does not degrade their quantitative predictions to any marked degree^{37,56,62}.

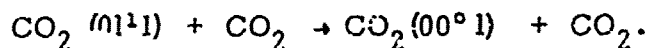
4. VIBRATION STATES CHOSEN FOR REVIEW AND PRELIMINARY RATE SCREENING

This review considers the first fourteen vibrational levels of CO_2 , the first five of water as well as the first two or three states of several of the more prominent diatomic species. The vibrational species considered are all tabulated in Table I along with their normal frequencies. Data for CO_2 and H_2O were taken from Courtoy³⁸ and Herzberg³⁹ resp., whereas, the results for all diatomics considered were found in the JANAF Thermochemical Tables⁶⁵.

In a preliminary effort to screen the deactivation rates down to a collection of tractable size, the rates of formation for all products that are created by deactivation of a given vibrational species were compared for relative magnitude at each of several temperatures up to 3000°K . Frequently, only one or two products were found to be favored almost to the exclusion of all others. This allowed for a ready selection of favored paths, the others being dropped from further consideration. This procedure was repeated for each of the several catalysts considered. As an example of this procedure, we present the following case:



The rates of formation for 9 different products are illustrated in Table II for a temperature of 1500°K . A survey of this table shows that only the following deactivation rate need be considered in this instance:



Similar results were obtained over the entire temperature range. Accordingly, $\text{CO}_2(00^01)$ is the only product of V-T deactivation of $\text{CO}_2(01^11)$ by CO_2 that is further considered in the review. During the course of these computations, it was found that the relative amounts of the various products formed depended critically upon the temperature and only slightly upon the molecular weight of the catalyst. As a consequence, the basic conclusions drawn from Table II can be assumed to be general at 1500°K .

5. CURRENT STATUS OF EXPERIMENTAL RATES

Taylor and Bitterman (TB)¹ have published a very extensive review of most of the experimentally determined rates of interest to the current review. As a consequence, our first aim in this regard will be to update their review with any new data that may be available. Below, sixteen processes are discussed.



The most studied of all of the energy transfer classes considered in the present collection of rate data is that of process (i) with $\text{M}=\text{CO}_2$. Since the review of TB, the only significant study of this process was that published by Simpson et al¹⁵. Our selected rate is derived from a combination of these two sets of data. In a similar fashion, the rate for this process with $\text{M}=\text{N}_2$ as derived from a combination of the results of the same two sets of authors. In this overall analysis, we have found that the ratio $(k_{\text{N}_2}/k_{\text{CO}_2})$ changes from 0.66 at 360° K to only 0.72 at 1500° K. As a consequence, we assume that $k_{\text{N}_2} \sim 0.7k_{\text{CO}_2}$. Since CO and O₂ have molecular constants very similar to those of N₂, we assume that $k_{\text{O}_2} \sim k_{\text{N}_2} \sim k_{\text{CO}}$.

The rate of the above process with $\text{M}=\text{H}_2$ has also been reviewed by TB as well as in the experimental studies of Simpson and Chandler¹⁸. Although the amount of data present in this instance is far less than for the catalysts discussed above, sufficient data are available to allow for a determination of the temperature dependence of the process from 300° K up to 1100° K.

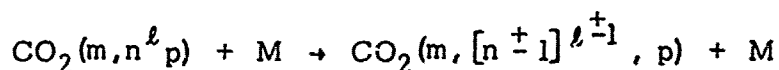
Water vapor is known to be an efficient catalyst¹ for the vibrational deactivation of $\text{CO}_2(01^1 0)$. As TB point out, there is considerable question about the actual mechanism of this process. The explanations vary from a qualitative explanation based upon the chemical affinity⁶⁶ between H_2O and CO_2 to form H_2CO_3 , to an explanation based upon an assumption of V-R exchange, made efficient by the hydride-like nature of H_2O , with an attendant small moment of

inertia⁵⁶, Sharma⁶⁸ has estimated the magnitude and temperature dependence of this process from multipole interaction theory and an assumption of V-R energy exchange. Although this rather sophisticated calculation does reproduce the magnitude of the data, it is difficult to choose it over the results of more simple models due to the high degree of scatter in the data available. Our rate for this process is based upon a combination of the very recent results of Buchwald et al³ and the results reviewed by TB. The two sets of data allow for a determination of the rate from below room temperature to above 1000°K.

Finally, the rate for M=H was considered from the standpoint of Herzfelds theoretical treatment for CO₂. In order to place the value for this rate in perspective, we have made theoretical calculations also for the case of M=H₂. Since the two calculations both exhibited nearly the same temperature dependence, the theory allowed for a determination of the ratio k_H/k_{H_2} .

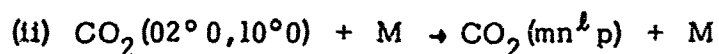
This value is reported in Table IIIa for process (i). The value for k_H is reported relative to k_{H_2} due to the fact that H₂ has a molecular weight near that for H and thus the theoretical expressions will have nearly the same temperature dependence making the two comparable over a wide range of conditions.

A close examination of equations (i) reveals that reactions of the type



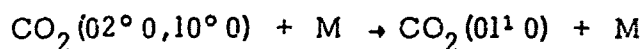
will have differences in rates due almost entirely to differences in the values of their statistical factors S. Consequently, within the approximation of the harmonic oscillator, statistical considerations alone are sufficient to relate the rates of these reactions to the experimentally derived results for process (i). A large number of rates considered in this review were evaluated in this manner.

A graphical review of experimentally derived rates for process (i) with various collision partners is illustrated in Fig. 1 and tabulated in Table III.

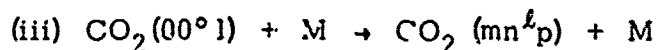


Attempts at modeling of the performance of CO₂ lasers usually involve an assumption that CO₂(10° 0) and CO₂(02° 0) are strongly coupled, i.e., they

are essentially in thermodynamic equilibrium. With this in mind, Rosser et al²² have performed experiments directed toward a measurement of the deactivation rate of $\text{CO}_2(10^\circ 0)$ in the presence of excess CO_2 as well as in the presence of H_2O . Their method involved the injection of excess vibrationally excited species into both laser levels, following which the approach to equilibrium by radiation at both 10.6μ and 4.3μ was monitored. They reported values of 1.87×10^{10} cc/mole-sec and 2.25×10^{12} cc/mole-sec for the rates of this process at 300°K with CO_2 and H_2O respectively as collision partners. Two deactivation products are possible for process (ii), i.e., $\text{CO}_2(01^1 0)$ and $\text{CO}_2(00^\circ 0)$. Actually, $\text{CO}_2(02^2 0)$ can also form; however, theory²² suggests that this form will be in near equilibrium with $\text{CO}_2(02^\circ 0, 10^\circ 0)$ even at room temperature. Theory²² further shows that at 300°K over 99% of the product will be $\text{CO}_2(01^1 0)$. As a consequence, we interpret these rates in terms of twice the rate of the following process:



The rate measured will be twice the rate of this process due to the degeneracy of the product. In the absence of further experimental results, resort was made to theory to obtain the dependence upon temperature for these rates. It is of interest to compare the above experimental constants with the values that can be estimated from statistical considerations and the measured rates for process (i). The statistical factor for this process is 2; accordingly, the predicted values for the rate constants at 300°K would be 6.6×10^9 and 1.7×10^{13} cc/mole-sec for CO_2 and H_2O respectively as collision partners. The actual value for CO_2 is larger by a factor of 1.5 than the predicted rate, whereas, the experimental value for H_2O is smaller by a factor of 14. At present, it is difficult to establish the source of this discrepancy. One possible source of error is the assumption that $\text{CO}_2(02^2 0)$ and $\text{CO}_2(02^\circ 0, 10^\circ 0)$ are always in near equilibrium.



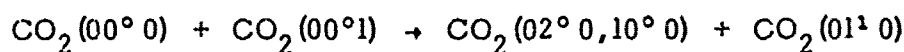
This process has lent itself readily to investigation by means of the technique of laser fluorescence in recent years¹⁻¹³. In addition, shock-tube studies have been conducted at elevated temperatures, and numerous measurements based upon methods of sound dispersion have been conducted at near

room temperature¹. We have added the data from recent laser fluorescence experiments^{3,6-13} to the results reviewed by TB and by least squares analysis obtained the results plotted in Fig. 2. Due to their wide variance from the results obtained by laser fluorescence techniques, we have ignored the results of Serikov¹², which were obtained by a phase method.

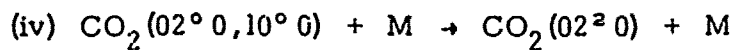
Six deactivation products are possible in the present instance: $\text{CO}_2(03^1 0, 11^1 0)$, $\text{CO}_2(03^3 0)$, $\text{CO}_2(02^0 0, 10^0 0)$, $\text{CO}_2(02^2 0)$, $\text{CO}_2(01^1 0)$, and $\text{CO}_2(00^0 0)$. The rate constant for the formation of each product was evaluated by means of the following relationship

$$k(i) = \left[\frac{k(i)}{\sum_i k(i)} \right]_{\text{Theory}} k_{\text{expt}}$$

where $k(i)$ is the rate constant for the formation of the i^{th} product. The term in the square brackets was evaluated with the aid of Herzfeld's development of the SSH theory for CO_2 ²². This analysis demonstrated that at temperatures below 3000°K only the products $\text{CO}_2(03^1 0, 11^1 0)$, $\text{CO}_2(02^0 0, 10^0 0)$ and $\text{CO}_2(01^1 0)$ need be considered. In addition, the following process was considered in the analysis and found to be of importance:



The results of these calculations are all presented in Table IIIa.

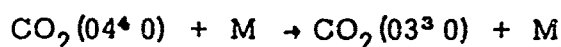


While there are several examples of class (iv) of near resonant transfers included in Tables IIIa and IIIb, at present there are no experimental data available upon which estimates of rates can be based. As a consequence, we resort entirely to available theory. The treatment given by Herzfeld²² indicates that processes of this type will always be in near equilibrium even at 300°K. Although the interpretation of the results of Rhodes et al⁶⁹ is open to

some questions concerning mechanism, their results seem to indicate that near resonant processes of this type are indeed rapid having rates not far removed from those given by theory^{1,22}.



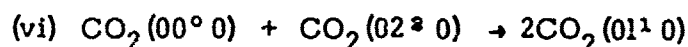
There are examples of several examples of class (v) type processes included in Table IIIa. The low rates of deactivations of this type in contrast to the rapid rates of processes of the type



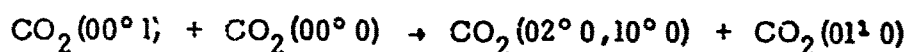
are due to the many individual steps involved in the overall case, i.e., we have in the present instance



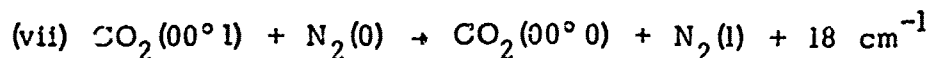
In reality, these multistep processes are slow and can be ignored except at the highest temperatures. This particular case is given merely as an example to illustrate the type of results obtained. The many steps required are the result of an application of the selection rules. No experimental data are available regarding multistep processes of this type making it necessary to rely entirely upon theory for useable estimates.



A large number of near resonant V-V transfers in CO_2 are included in the present review. In the absence of any conclusive experimental results, the rates of all of these processes have been estimated by theory²². From the results of Rhodes et al⁶⁹ above, the rate constant at 300°K was estimated at about 9×10^{12} cc/mole-sec in fair agreement with the value of 3.5×10^{12} cc/mole-sec given by theory. Since the results of Rhodes et al⁶⁹ are still open to discussion concerning interpretation, we have kept the theoretical value for our review. One nonresonant V-V transfer included in our review, i.e.,



was related by theory to rates given experimentally, see (iii) above.



Of all the intermolecular V-V exchanges between unlike molecules considered in this review, this process is the nearest to energy resonance, i.e., the energy defect is only 18 cm^{-1} . Because of the near resonance, available theory²² predicts a very rapid rate for the energy exchange. Indeed, it is known that this very rapid process is necessary to obtain inversion in the upper level population of the $\text{CO}_2\text{-N}_2$ laser system¹. Because of obvious parallelism between that system and the production of non-equilibrium radiation in exhaust plumes, this process can be expected to be very important in the latter case also.

Extensive experimental data are available regarding V-V transfers from $\text{CO}_2(00^{\circ}1)$ to both $\text{N}_2(0)$ and $\text{CO}(0)$ ^{8,10,14,16,17}. The methods used to obtain these data involve primarily laser fluorescence^{8,10,14} and shock tube techniques^{16,17}. We have included all of the data from these sources in our analysis, the net result of which is illustrated in Fig. 4.

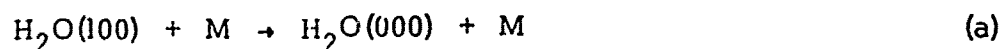


Water is known to have an extremely fast self relaxation time³³⁻³⁶; the probability for self deactivation per collision exceeding $1/5$ at room temperature¹. Data are available relative to this process for $\text{M}=\text{H}_2\text{O}$ from one impact tube study³³ and three sound-dispersion studies³⁴⁻³⁶. The data available are somewhat scattered making it difficult to establish the temperature dependence, as shown in Fig. 5.

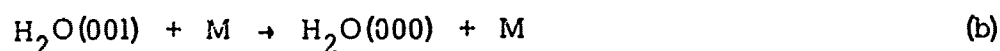
In an effort to estimate the temperature dependence, we have resorted to the theories of Shin^{37,70}. Shin has developed two sets of classical equations which treat this process as a V-T exchange in one instance and a V-R-T exchange in the second case. Although the two approaches appear to give a markedly different character to the temperature dependence, they both reproduce the absolute

magnitude of the data reasonably well. The different types of temperature dependencies may be an illusion due to the failure to account for multipole attractive terms in the latter (V-R-T) case. Since the theoretical development of the V-T case has been more complete, and since this case does appear to reproduce the available data measureably better, we have selected the V-T method to provide information for our collection of rates.

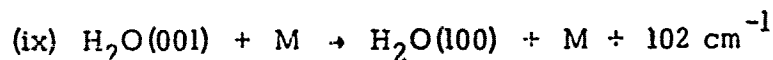
At present no data are available regarding the efficiency of other collision partners relative to this process. In the absence of required data, we have resorted to Shin's³⁷ classical V-T theory in all cases considered. This theory was also used for the following related processes:



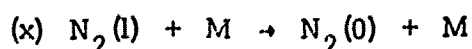
and



No experimental data are available regarding the rates of these processes making a complete resort to theory necessary; however, the success of the theory in giving rates for (viii) above leads us to accept the results with some degree of confidence.



No data are currently available regarding the rates of intramolecular V-V energy exchanges in water. In the absence of such data, we have resorted to the SSH theory⁶¹. As is to be expected for near resonant transfers of this type, the predicted rates approach collision frequency. We did not use the theories of Shin^{37,70} here due to the fact that they have not been designed to expressly handle V-V transfers in the stepwise fashion built into the SSH theory, i.e., they do not account for seemingly important quantum effects that appear in this class of transfers.



The deactivation of N_2 by itself has been extensively studied in the shock tube at elevated temperature (above 1200°K)⁷¹⁻⁷⁴. In addition, data are available from sound absorption and dispersion studies^{75,76} and one impact tube study⁷⁷, all at lower temperatures (below 1200°K). Unfortunately, as has been pointed out by TB only the shock-tube data appears self consistent, the rest being widely scattered. In accordance with the conclusions of TB, we assume this scatter to be due to impurities, the effects of which would be greatly magnified by the inordinately slow relaxation time at lower temperatures. Our selection of rate data are therefore taken only from the shock tube results⁷¹⁻⁷⁴.

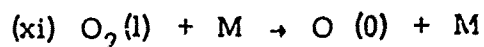
Henderson⁷⁸ has reported measurements based upon sound absorption which show CO_2 having an efficiency nearly 3 orders of magnitude greater than that of N_2 in this process. However, his interpretations of the results of his experiments are open to question^{1,78}. As TB in their review point out, Henderson's results are surprising in that CO_2 and N_2 show very similar efficiencies in other processes. In the absence of further data, we have resorted to theory²² to estimate the efficiency of CO_2 for the purpose of this review.

Water is known to efficiently relax most diatomic molecules¹. The data of Huber et al⁷⁷ and TB show no exception to this rule. These two studies cover a temperature range from 413 to 1600°K and involve impact tube as well as shock-tube techniques. Our rates for the relaxation of $\text{N}_2(l)$ by H_2O are taken from the total collection of these two sets of data.

White⁷⁹ has investigated the relaxation of $\text{N}_2(l)$ by H_2 at temperatures above 1500°K . Although the data are limited and cover only a narrow temperature range, we have used them to estimate rates for this system. The required temperature dependence was taken from theory²².

Finally, deactivation rates for $\text{N}_2(l)$ by O_2 , CO , and H were evaluated directly from theory²². In the case of H , we have evaluated only the ratio $(k_{\text{H}}/k_{\text{H}_2})$

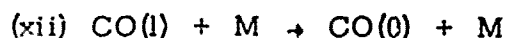
from theory and used the reported values of k_{H_2} to determine k_H . The deactivation rates for process (x) which were taken from experimental studies are all illustrated in Fig. 6.



Like process (x), the self deactivation of oxygen has been extensively studied. The data have been reviewed by TB and cover a temperature range of nearly 10,000° K. Furthermore, the experimental results were found to be in excellent agreement with theory (SSH)⁶¹ over the entire temperature range. Our rate constants were taken from that compilation.

Henderson et al⁵ have conducted sound absorption studies in $\text{O}_2\text{-H}_2\text{O}$ systems and estimate a value for the deactivation rate constant of $\text{O}_2(l)$ by H_2O at 300° K of $k_{H_2O} \leq 2.9 \times 10^{10}$ cc/mole-sec. We have accepted this value in the absence of further experimental data and supplied to it the temperature dependence reported for the deactivation of $\text{N}_2(l)$ by H_2O .

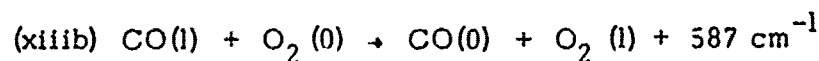
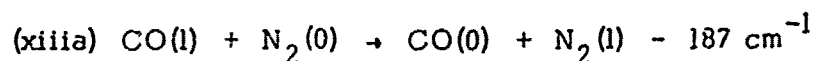
Very little data are available regarding the deactivation of $\text{O}_2(l)$ by other collision partners. Henderson et al⁸⁰ claim evidence based upon sound absorption studies that CO_2 is nearly 3 orders of magnitude more efficient than O_2 in the relaxation of O_2 ; however, their conclusions have been the subject of some argument and will not be considered further. As TB point out, O_2 , N_2 , and CO_2 exhibit similar efficiencies in numerous deactivation processes and it would be surprising to find either O_2 or N_2 to be so much less efficient than CO_2 in these processes. Furthermore, neither N_2 nor O_2 exhibit unusual efficiencies in the deactivation of vibrationally excited CO_2 . As a consequence, we rely upon the SSH theory^{22, 61} to estimate the rate of deactivation of $\text{O}_2(l)$ by CO_2 , H_2 , and H . All deactivation rate constants which were taken from experimental results are illustrated in Fig. 7.



Since CO is infrared active with a spectral region which overlaps 4.3 μ band of CO_2 , an adequate description of the radiation emitted by a plume at these wavelengths requires a knowledge of the concentrations of excited CO. This vibrational deactivation process (xii) has been extensively studied in the shock tube over a wide range of experimental conditions and in the presence of several collision partners²⁴⁻²⁸. Hooker et al²⁷ have conducted the most extensive studies of this process to date. They measured the deactivation

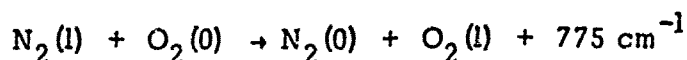
rate in the presence of N_2 and H_2 , as well as CO itself. The results of Matthews²⁴, Gaydon et al²⁵, and Windsor et al²⁶ were combined with the results of Hooker et al to give an averaged rate constant for $M=CO$. The results for $M=N_2$ and $M=H_2$ were taken directly from Hooker et al²⁷. The rates of (12) for $M=H_2O$ were taken directly from the shock tube results of Von Rosenberg et al⁴⁰.

This system is the only one considered in this review for which data are available concerning the deactivation rate in the presence of H atoms³². The relaxation was studied under conditions of rapid nonequilibrium expansion, a shock tunnel being used to generate a nozzle flow with stagnation temperatures up to $4500^\circ K$. The effect of H atoms was determined by adding trace amounts of H_2 to the initial gas mixture. The catalytic efficiency of H in this process is very high, the rate approaching collision frequency at temperatures above $2000^\circ K$. The reported steep temperature dependence for this system may be a result of the method of H atom generation; i.e., the dissociation rate of H_2 itself is very temperature dependent. Furthermore, the concentration of H was not monitored. Nevertheless, the SSH theory^{22,61} does reproduce the dependence upon temperature very well and only underestimates the rate constant by about a factor of three. Thus, at $1500^\circ K$ theory gives a value of 4×10^{12} cc/mole-sec; whereas, experiment gives a value of 1×10^{13} cc/mole-sec. The rate constants for this system which were based upon experimental observation are illustrated in Fig. 8.



Sato et al²⁸ have applied shock tube techniques to the study of vibrational energy transfers of the above type between several pairs of diatomic molecules. In both cases, they covered a temperature range of 1500° to $2500^\circ K$. In addition to this study, Bauer et al²⁹ have studied (xiiib) at room temperature by means of a sound dispersion technique. It is of interest to note that in both of these cases, Sato et al²⁸ demonstrated that the SSH theory^{22,61} agrees with experiment to a factor of two over the whole temperature range.

Also of interest to the present review and of the same general class as (xiii) is the following process:

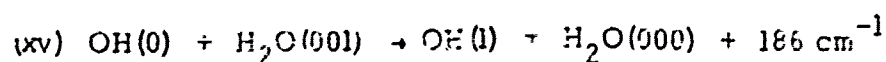


Bauer and Roesler²⁹ have estimated the rate of this process at 300°K from sound dispersion measurements on N₂-O₂ mixtures. All other studies of this system were conducted with shock tubes at elevated temperatures⁸¹⁻⁸³. The experimentally derived rate constants for the last three processes are illustrated in Fig. 9.



The inclusion of the hydroxyl radical into our model appears warranted due in part to its possible near resonant transfer of energy into and out of the stretching modes of the water molecule. This process has not been studied directly; however, Worley, Coltharp, and Potter⁸⁴ have studied the rates of deactivation of OH(9) by several diatomic and small polyatomic molecules. The rate constants ($k \times 10^{-10} \text{ cm}^3/\text{mole-sec}$) of interest to the present review and which were measured were (k,M):(0.6, O₂); (0.2, N₂); (1.4, CO₂); (12, H₂O) at 300°K.

In the absence of definitive results regarding the deactivation of OH(l) by different M, we have proceeded as follows. First, the self deactivation rate (M=OH) was estimated from the classical equations of Shin⁴² which treat the case of the self catalyzed deactivation of a diatomic hydride (V-R-T). The harmonic oscillator approximation is then used to estimate $k(l \rightarrow 0)$ from the measured rate $k(9 \rightarrow 8)$ for each M of interest. The temperature dependence in each case was estimated with the aid of Shin's³⁷ equations for V-T transfer. It is interesting to note that for a temperature of 300°K, the theory estimates $k(l \rightarrow 0)$ at $3.6 \times 10^3 \text{ cc/mole-sec}$ for M=N₂, whereas, the harmonic oscillator approximation relative to the data of Worley et al⁸⁴ places the value at $5.5 \times 10^3 \text{ cc/mole-sec}$. The transition matrix element required by the theory for the internal vibrational coordinate of OH(l) was taken from the estimates of Potter et al⁸⁵ relative to their measurements of lifetimes for OH(9). In the absence of experimental data relative to CO as a collision partner, we rely entirely upon theory³⁷ for its efficiency in relationship to that of N₂, see Table IIIe.



Intermolecular energy transfer rates (V-V) between the vibrational modes of H_2 and OH and the stretching modes of H_2O were estimated from the SSH theory^{22,61}. According to theory, these exchanges are all very efficient having probabilities in the neighborhood of 0.1 or higher at 1500° K. In reality, assumptions made in the theoretical model preclude accurate predictions at these levels of efficiency; nevertheless, the order of magnitude can probably be trusted. Significantly, the equations of Shin^{42,62,70} which treat the transfer of vibrational energy into the rotational modes (V-R-T) of hydrogen containing molecules also predict very high deactivation efficiencies. Nevertheless, we have selected rates based upon the SSH theory for these V-V transfers due to the important quantum considerations discussed under (ix) above.

The transfer of vibrational energy between $\text{H}_2(1)$ and OH(0) was treated in a manner analogous to that described above and is reported in Table IIIe.



The vibrational relaxation of H_2 has been the subject of numerous experimental investigations in recent years. Unfortunately, little is known regarding the efficiencies of collision partners other than H_2 itself. The relaxation has been studied in detail at elevated temperatures in shock tubes^{57,86}. More recently studies have been reported regarding measurements at near room temperature. These involve the use of stimulated Raman scattering^{58,59} and somewhat indirectly, laser fluorescence⁸⁷. Our self deactivation rate for H_2 was derived from the sum of these experimental results which cover a temperature range from 296° K to 2700° K. The resultant rate constant is illustrated in Fig. 10 as a function of temperature.

In the absence of experimental results, the efficiencies of N_2 , CO, O_2 , CO_2 , H_2O , and H all relative to H_2 were estimated from the SSH theory. The results have been entered into the table of rate data.

6. SUMMARY

Available rate data derived from experimental studies have been combined with results derived from current theory to provide a fairly extensive model of vibrational energy transfer for the $\text{CO}_2\text{-N}_2\text{-CO-H}_2\text{O}$ system. Based upon the data compiled in this effort, several generalizations can be made.

As pointed out by Taylor and Bitterman¹, there is a large amount of experimental data available regarding the deactivation (V-T) of $\text{CO}_2(01^10)$ during $\text{CO}_2\text{-CO}_2$ collisions. This state of affairs proves very fortunate due to the large number of rates that can be related statistically to the magnitude of the rate for this one process. It is disconcerting to find that contrary to available theory²², N_2 and O_2 appear experimentally to be slightly less efficient catalysts in this process than CO_2 . At the time Taylor and Bitterman¹ published their review, the efficiency of N_2 in this process was known primarily from highly scattered results derived from the spectrophone at or near room temperature. We have selected the more recent results of Simpson et al¹⁵ which show less scatter and cover a much broader temperature range. Experimental studies regarding the efficiencies of H_2O and H_2 as collision partners in process (i)* have also recently appeared^{3,18}. Overall, our knowledge of the parameters important in these processes is probably satisfactory.

The recent advent of the study of vibrational deactivation by the technique of laser fluorescence has proven very useful as a tool for studying the deactivation of the asymmetric stretching mode of CO_2 ^{3,8,10,11,13,14}.

Indeed, the efficiencies of $\text{CO}_2, \text{H}_2\text{O}, \text{N}_2, \text{O}_2, \text{CO}$, and H_2 as collision partners in this process have all been determined by this technique. The results available from these investigations normally cover a temperature range of 298° up to 1000°K . Where possible, the temperature range has been extended for this review by inclusion of shock-tube data taken at elevated temperatures. It appears that our knowledge of the efficiencies of important collision partners relative to deactivation of the asymmetric stretching mode is quite adequate for the modeling purposes intended herein.

*See Section 5 for a review of process (i).

The same technique of laser fluorescence has been used to characterize the intermolecular transfer of vibrational energy between $\text{CO}_2(00^01)$ and $\text{N}_2(0)$ as well as $\text{CO}(0)$. Both of these processes seem to have been adequately studied by this technique^{10,14}. In addition, the transfers to $\text{N}_2(0)$ have been extensively studied in the shock-tube at elevated temperatures. Sharma and Brau⁶⁴ have reproduced these experimental results in a very satisfactory manner theoretically. Although their quantum theoretical model appears quite capable of reproducing experimental results for energy transfers in CO_2 to at least as good an approximation as the SSH theory²², as pointed out earlier, it was judged more involved than the present review justifies.

Theory²² indicates that near resonant intramolecular V-V transfers of the type



occur with very high probabilities per collision ($P > .01$). At present, the only experimental evidence available regarding these processes is that of Rhodes et al⁶⁹ which lends support to these theoretical predictions. Nevertheless, the interpretation of these results is still open to question. If processes of this type are indeed as fast as now appears likely, modeling problems involving CO_2 can be greatly simplified by assuming that states with the same value for the quantum number v_2 but different quantum numbers l are in near equilibrium. This is equivalent to ignoring the quantum number l altogether. If this approach were followed, the number of vibrational transfers that would need to be considered would be greatly reduced. We offer Table IV, which contains a fairly complete set of intermolecular V-V exchanges among CO_2 molecules, as an example of this approach.

At present, our knowledge of the vibrational relaxation rate for H_2O is very limited and the data are very scattered (see Fig. 5). In addition, our knowledge is limited further to the efficiency of only one collision partner, H_2O itself, and then only for the relaxation of the bending mode. Much experimental data is yet needed for this system in view of the remarkable effect H_2O has upon the vibrational lifetimes of other molecules. Work in progress at AVCO Corporation is directed toward a satisfaction of some of these needs⁸⁹.

Finally, our knowledge of the effect of reactive atomic species upon the relaxation rates of important vibrational states in the system under consideration is at present limited to the single study of Von Rosenberg et al.³² regarding the effect of H atoms upon the relaxation rate of CO(l) and the preliminary results of Center⁹⁰ concerning the effect of atomic oxygen upon the relaxation rate of CO₂(01¹0). Interestingly enough, in both instances it was found that these reactive atoms significantly reduce the vibrational lifetimes. Center⁹⁰ finds that O-atoms are about four times more efficient than CO₂ in relaxing CO₂(01¹0). Much work needs to be done in this area if the atomic species are as efficient as it now appears.⁹⁴

7. EXPLANATION OF THE TABLE OF RATE DATA

All rate data, experimentally or theoretically derived, was expressed as a power series in temperatures, $T^{\circ}\text{K}$, as follows:

$$\ln k = A + BT^{-1/3} + CT^{-2/3}$$

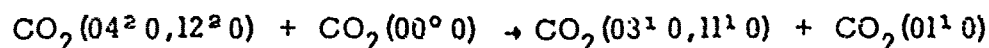
The constants A, B, and C were entered into the table. In addition, the rate constant taken directly from its source and corresponding to a temperature of 1500°K was entered.

Frequently it was possible to relate a group of rate constants to one another by means of the relative efficiencies of the collision partners involved. This treatment was possible only when the temperature dependencies of the constants involved were similar. The column headed by the symbol ϕ refers to these relative efficiencies. The efficiency factor ϕ is measured relative to the rate for which it is set equal to unity unless otherwise specified in the table.

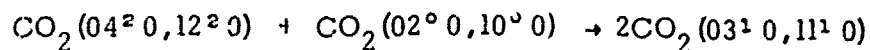
Sometimes processes occur which have two equal energy paths, but with different values of Z_0/S for each path. In this situation the rate is the sum of the rate for each path and both values of Z_0/S and shown in the Tables.

Finally, the source of each rate, theoretical or otherwise, is listed in the last column as a reference or series of references. Molecular transport properties used in this study to evaluate the theoretical rate processes by the methods presented in section 3 were taken from Hirschfelder, Curtis, and Bird⁹¹, except for the H atom properties which were taken from Svehla⁹².

When using the table of rate data provided herein, it is useful to keep in mind that at equilibrium the concentration of an excited molecular species relative to the concentration of the ground state falls off at higher energy levels according to the Boltzman factor ($e^{-\Delta E/RT}$). As a consequence, for conditions not far removed from equilibrium the process



will be more likely to be of importance than the process



simply due to the fact that the concentration of $\text{CO}_2(00^0 0)$ is likely to be much greater than that of $\text{CO}_2(02^0 0, 10^0 0)$ below 1500°K . As the temperature increases, however, the number of individual states and thus the complexity of the mechanism must necessarily increase.

Included as Table V are the Einstein coefficients for spontaneous emission which give rise to the vibration/rotation infrared spectra of CO_2 , CO , and H_2O .

8. TABLES

- I. Vibrationally Excited Species and Energy Levels.
- II. Product Formation Rates for the Following Process:
 $\text{CO}_2 (01^11) + \text{CO}_2 \rightarrow \text{CO}_2 (mn^k p) + \text{CO}_2.$
- IIIa. V-T Intramolecular V-V Energy Transfers in $\text{CO}_2.$
- IIIb. Intermolecular V-V Energy Transfer Rates in $\text{CO}_2.$
- IIIc. Scrambling Reactions in $\text{CO}_2.$
- IIId. V-T and Intramolecular V-V Energy Exchanges in Species Other Than $\text{CO}_2.$
- IIIe. Intermolecular V-V Transfer Involving Species Other Than $\text{CO}_2.$
- IVa. Alternate Table of Resonant Intermolecular V-V Energy Exchange Rates Among CO_2 Molecules.
- IVb. Resonant Intermolecular V-V Energy Exchange Rates Between Symmetric Stretching Modes of CO_2 Molecules.
- V. Einstein Coefficients For Spontaneous Emission.

TABLE I
VIBRATIONALLY EXCITED SPECIES AND ENERGY LEVELS

States	$\omega(\text{cm}^{-1})$	ω (Average)	$\Delta H(\text{Kcal/mole})^*$
$\text{CO}_2(01^10)$	667.4	667.4	1.908
$\text{CO}_2(02^00, 10^00)^{'}$	1285.4	1336.8	3.821
$\text{CO}_2(02^00, 10^00)^{''}$	1388.2		
$\text{CO}_2(02^20)$	1335.2	1335.2	3.817
$\text{CO}_2(03^10, 11^10)^{'}$	1932.5	2004.7	5.730
$\text{CO}_2(03^10, 11^10)^{''}$	2076.9		
$\text{CO}_2(03^30)$	2003.3	2003.3	5.726
$\text{CO}_2(00^01)$	2349.2	2349.2	6.715
$\text{CO}_2(04^00, 12^00, 20^00)^{'}$	2548.2	2672.0	7.638
$\text{CO}_2(04^00, 12^00, 20^00)^{''}$	2670.8		
$\text{CO}_2(04^00, 12^00, 20^00)^{'''}$	2797.0		
$\text{CO}_2(04^20, 12^20)^{'}$	2584.9	2672.9	
$\text{CO}_2(04^20, 12^20)^{''}$	2760.8		
$\text{CO}_2(04^40)$	2672.8	2672.8	7.640
$\text{CO}_2(01^11)$	3004.1	3004.1	8.587
$\text{CO}_2(05^10, 13^10, 21^10)^{'}$	3181.3	3340.9	9.546
$\text{CO}_2(05^10, 13^10, 21^10)^{''}$	3339.3		
$\text{CO}_2(05^10, 13^10, 21^10)^{'''}$	3502.0		
$\text{CO}_2(05^30, 13^30)^1$	3241.5	3342.2	9.550
$\text{CO}_2(05^30, 13^30)^{12}$	3442.9		
$\text{CO}_2(05^50)$	3341.8	3341.8	9.549

$$* \Delta H = \frac{hc}{k} \frac{R}{10^3} \omega_{\text{ave}}$$

where k = Boltzman's constant

$$\frac{hc}{k} = 1.439 \text{ cm} \cdot ^\circ\text{K}$$

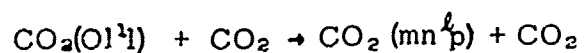
$$R = 1.987 \text{ cal} \cdot ^\circ\text{K}^{-1} \cdot \text{mole}^{-1}$$

TABLE I (Cont.)

States	$\omega(\text{cm}^{-1})$	$\Delta H(\text{Kcal/mole})$
H ₂ O(O1O)	1595.0	4.559
H ₂ O(O2O)	3151.4	9.008
H ₂ O(100)	3651.7	10.438
H ₂ O(001)	3755.8	10.736
N ₂ (1)	2329.5	6.659
N ₂ (2)	4630.7	12.238
O ₂ (1)	1556.1	4.448
O ₂ (2)	3088.1	8.828
H ₂ (1)	4154.7	11.876
CO(1)	2142.6	6.125
CO(2)	4258.3	12.173
OH(1)	3682.	10.526

TABLE II

Product Formation Rates* for the Following Process:



Product	k(1500°K)	% Formed
(04 ⁴ 0)	8.9×10^4	--
(04 ² 0, 12 ² 0)	2.2×10^9	.07
(04 ⁰ 0, 12 ⁰ 0, 20 ⁰ 0)	2.9×10^9	.09
(00 ⁰ 1)	3.1×10^{12}	99.8
(03 ¹ 0, 11 ¹ 0)	1.5×10^8	--
(03 ² 0)	7.2×10^5	--
(02 ⁰ 0, 10 ⁰ 0)	1.5×10^6	--
(02 ² 0)	1.6×10^6	--
(01 ¹ 0)	2.1×10^6	--

* Calculations based upon the theory of Herzfeld²² and known rates for the deactivation of $\text{CO}_2(01^10)$ by CO_2 .

TABLE III a
V-T AND INTRAMOLECULAR V-V ENERGY TRANSFERS IN CO₂

REACTION	M	ϕ	A	B	C	k(1500°K)	SOURCE
(01 ¹ 0) → (00 ⁰ 0)	CO ₂	1.0	38.3	-177	451	2.5×10 ¹¹	1,15
	N ₂ , O ₂ , CO	0.7				1.8×10 ¹¹	1,15
	H ₂		33.0	-83.0	345	2.2×10 ¹³	18
	H ₂ O		31.0	-44.4	242	3.8×10 ¹³	1,3
	H	0.9 [‡]				1.9×10 ¹³	22
(02 ⁰ 0, 10 ⁰ 0) → (01 ¹ 0)	CO ₂	1.0	39.3	-177	451	7.0×10 ¹¹	1,15,23
	N ₂ , O ₂ , CO	0.7				4.9×10 ¹¹	1,15,23
	H ₂ O		29.0	-44.4	242	5.0×10 ¹¹	1, 3,23
	H ₂		33.0	-83.0	345	2.2×10 ¹³	18,22
	H	0.9 [‡]				2.0×10 ¹³	22
(02 ⁰ 0, 10 ⁰ 0) → (00 ⁰ 0)	CO ₂	1.0	34.1	-137		4.1×10 ⁹	22,23
	N ₂ , O ₂ , CO	3.1				1.3×10 ¹⁰	22
	H ₂ O		26.8	-44.0	242	6.2×10 ¹⁰	22,23
	H ₂		39.5	-149	451	1.0×10 ¹³	22
	H	1.6 [‡]	38.4	-131	446	1.6×10 ¹³	22
(02 ² 0) → (01 ¹ 0)	CO ₂	1.0	39.0	-177	451	5.1×10 ¹¹	1,15,2
	N ₂ , O ₂ , CO	0.7				3.6×10 ¹¹	1,15,22
	H ₂		33.7	-83.0	345	4.4×10 ¹³	18,22
	H ₂ O		31.7	-44.4	242	7.6×10 ¹³	1, 3,22
	H	0.9 [‡]				4.0×10 ¹³	22
(02 ⁰ 0, 10 ⁰ 0) → (02 ² 0)	CO ₂	1.0	36.5	-88.9	226	1.6×10 ¹²	27
	N ₂ , O ₂ , CO	0.9				1.5×10 ¹²	22
	H ₂	0.13				2.1×10 ¹³	22
	H ₂ O	0.				5.3×10 ¹²	22
	H	0.				1.6×10 ¹³	22
(03 ¹ 0, 11 ¹ 0) → (02 ² 0)	CO ₂	1.0	39.4	-177	451	7.6×10 ¹¹	1,15,22
	N ₂ , O ₂ , CO	0.7				5.3×10 ¹¹	1,15,22
	H ₂		34.1	-83.0	345	6.3×10 ¹³	18,22
	H ₂ O		32.1	-44.4	242	1.1×10 ¹³	1, 3,22
	H	0.9 [‡]				5.6×10 ¹³	22
(03 ¹ 0, 11 ¹ 0) → (02 ⁰ 0, 10 ⁰ 0)	CO ₂	1.0	39.7	-177	451	1.0×10 ¹²	1, 3,22
	N ₂ , O ₂ , CO	0.7				7.0×10 ¹¹	1,15,22
	H ₂		34.4	-83.0	345	8.5×10 ¹³	18,22
	H ₂ O		32.4	-44.4	242	1.5×10 ¹³	1, 3,22
	H	0.9 [‡]				7.7×10 ¹³	22
(03 ¹ 0, 11 ¹ 0) → (01 ¹ 0)	CO ₂	1.0	34.1	-137		4.1×10 ⁹	22,23
	N ₂ , O ₂ , CO	3.1				1.2×10 ¹⁰	22
	H ₂		39.5	-149	451	1.0×10 ¹³	22
	H ₂ O		43.0	-234	525	3.5×10 ¹¹	22
	H	1.6 [‡]	38.4	-131	446	1.6×10 ¹³	22
(03 ³ 0) → (02 ² 0)	CO ₂	1.0	39.4	-177	451	7.5×10 ¹¹	1,15,22
	N ₂	0.7				5.3×10 ¹¹	1,15,22
	H ₂		34.1	-83.0	345	6.6×10 ¹³	18,22
	H ₂ O		32.1	-44.4	242	1.1×10 ¹³	1, 3,22
	H	0.9 [‡]				6.0×10 ¹³	22

TABLE III a (continued)

REACTION	M	σ	A	B	C	k(1500°K)	SOURCE
(03 ⁰ 0) → (02 ⁰ 0, 10 ⁰ 0)	CO ₂	1.0	31.5	-171	264	1.2×10 ⁸	22
	N ₂	1.8	31.1	-159	260	2.1×10 ⁸	22
	H ₂		27.5	-90.1	230	1.9×10 ⁹	22
	H ₂ O		27.5	-90.1	230	1.9×10 ⁹	22
	H	1.0	35.8	-244	934	1.9×10 ⁹	22
(03 ¹ 0, 11 ¹ 0) → (03 ⁰ 0)	CO ₂	1.0	37.2	-89.3	227	3.2×10 ¹³	22
	N ₂ , O ₂ , CO	0.9				2.8×10 ¹³	22
	H ₂	0.12				3.9×10 ¹³	22
	H ₂ O	0.33				1.1×10 ¹³	22
	H	0.094	34.5	-84.5	213	3.0×10 ¹³	22
(00 ⁰ 1) → (02 ⁰ 0, 10 ⁰ 0)	CO ₂	1.0	54.6	-404	1096	1.4×10 ¹²	1,3, 8,13,22
	N ₂ , CO	0.3				5.2×10 ¹¹	1,3, 8,10,22
	O ₂	0.4				5.6×10 ¹¹	11,22
	H ₂		46.5	-279	892	3.8×10 ¹³	3,10,13,22
	H ₂ O		27.9	+18.5	-211	1.3×10 ¹²	6,9,10,12,22
	H	1.5 [†]				7.2×10 ¹²	22
(00 ⁰ 1) → (03 ¹ 0, 11 ¹ 0)	CO ₂	1.0	43.6	-252	685	4.3×10 ¹¹	1,3, 8,13,22
	N ₂ , CO	0.3				1.3×10 ¹¹	1,3, 8,10,22
	O ₂	0.4				1.7×10 ¹¹	11,22
	H ₂		44.2	-293	914	1.3×10 ¹¹	3,10,13,22
	H ₂ O		19.3	+108	-397	1.5×10 ¹¹	6,9,10,12,22
	H	0.8 [†]				1.4×10 ¹¹	22
(00 ⁰ 1) → (00 ⁰ 0) → (01 ⁰ 0, 10 ⁰ 0) → (01 ¹ 0)	CO ₂		44.0	-242	633	6.1×10 ¹¹	1,3, 8,10,22
(00 ⁰ 1) → (01 ¹ 0)	CO ₂	1.0	53.9	-407	824	6.4×10 ¹⁰	1,3, 8,10,22
	N ₂ , CO	0.3				1.8×10 ¹¹	1,3, 8,10,22
	O ₂	0.4				2.4×10 ¹¹	11,22
	H ₂		47.9	-324	1033	9.6×10 ¹¹	3,10,13,22
	H ₂ O		30.7	-54.7	-36.0	1.3×10 ¹¹	6,9,10,12,22
	H	1.9 [†]				1.9×10 ¹²	22
(04 ⁰ 0, 12 ⁰ 0, 20 ⁰ 0) → (00 ⁰ 1)	CO ₂	1.0	30.0	-108	165	3.2×10 ⁹	22
	N ₂ , CO, O ₂	1.2	29.6	-100	161	3.8×10 ⁹	22
	H ₂		28.6	-63.5	45.2	2.1×10 ¹⁰	22
	H ₂ O		29.1	-65.3	159	8.7×10 ⁹	22
	H	0.8 [†]	26.3	-21.8	-101	1.6×10 ¹⁰	22
(04 ⁰ 0, 12 ⁰ 0, 20 ⁰ 0) → (03 ² 0)	CO ₂	1.0	30.2	-171	264	3.1×10 ⁷	22
	N ₂ , CO, O ₂	1.8				5.6×10 ⁷	22
	H ₂		29.6	-153	520	6.5×10 ⁸	22
	H ₂ O						
	H	0.9 [†]	32.8	-197	687	5.9×10 ⁸	22
(04 ⁰ 0, 12 ⁰ 0, 20 ⁰ 0) → (03 ¹ 0, 11 ¹ 0)	CO ₂	1.0	40.1	-177	451	1.5×10 ¹³	1,15,22
	N ₂ , CO, O ₂	0.7				1.1×10 ¹³	1,15,22
	H ₂		34.8	-83.0	345	1.3×10 ¹³	18,22
	H ₂ O		32.8	-44.4	242	2.3×10 ¹³	1, 3,22

TABLE III a (continued)

REACTION	M	ϕ	A	B	C	$\kappa(1500^\circ\text{K})$	SOURCE
(34°0, 12°0, 20°0) → (02°0, 10°0)	CO ₂	1.0	43.7	-272	437	1.4×10 ¹⁰	22
	N ₂ , O ₂ , CO	3.0	43.3	-254	433	4.3×10 ¹⁰	22
	H ₂		38.8	-134	371	1.0×10 ¹²	22
	H ₂ O		42.2	-215	430	3.7×10 ¹¹	22
	H	1.6†	37.7	-116	366	1.6×10 ¹³	22
(04°0, 12°0, 20°0) → (02°0)	CO ₂	1.0	39.2	-271	438	1.6×10 ⁸	22
	N ₂ , O ₂ , CO	3.1	38.8	-253	434	5.0×10 ⁸	22
	H ₂		34.6	-133	372	1.7×10 ¹¹	22
	H ₂ O		38.0	-214	431	6.2×10 ⁹	22
	H	1.6†	33.5	-114	366	2.7×10 ¹¹	22
(04°0, 12°0) → (04°0, 12°0, 20°0)	CO ₂	1.0	38.1	-90.4	230	7.2×10 ¹³	22
	N ₂ , O ₂ , CO	0.9	38.0	-90.8	231	6.4×10 ¹³	22
	H ₂	0.12	35.6	-84.9	214	8.6×10 ¹²	22
	H ₂ O	0.33	36.7	-88.3	237	2.4×10 ¹³	22
	H	0.09	35.3	-84.5	213	6.5×10 ¹²	22
(04°0, 12°0) → (03°0)	CO ₂	1.0	39.7	-177	451	1.0×10 ¹²	1, 15, 22
	N ₂ , O ₂ , CO	0.7				7.0×10 ¹¹	1, 15, 22
	H ₂		34.4	-83	345	8.5×10 ¹²	18, 22
	H ₂ O		32.4	-44.4	242	1.5×10 ¹³	1, 3, 22
	H	0.9†				7.7×10 ¹²	22
(04°0, 12°0) → (03°0, 11°0)	CO ₂	1.0	40.1	-177	451	1.5×10 ¹²	1, 15, 22
	N ₂ , O ₂ , CO	0.7				1.1×10 ¹²	1, 15, 22
	H ₂		34.8	-83.0	345	1.3×10 ¹³	13, 22
	H ₂ O		32.8	-44.1	242	2.3×10 ¹³	1, 3, 22
	H	0.9†				1.2×10 ¹³	22
(04°0, 12°0) → (04°0)	CO ₂	1.0	37.8	-90.4	230	5.4×10 ¹³	22
	N ₂ , O ₂ , CO	0.9	37.7	-90.8	231	4.8×10 ¹³	22
	H ₂	0.12				6.5×10 ¹²	22
	H ₂ O	0.33				1.8×10 ¹³	22
	H	0.09	35.0	-84.5	213	4.9×10 ¹²	22
(04°0) → (03°0)	CO ₂	1.0	39.7	-177	451	1.0×10 ¹²	1, 15, 22
	N ₂ , O ₂ , CO	0.7				7.0×10 ¹¹	1, 15, 22
	H ₂		34.4	-83.0	345	8.5×10 ¹²	18, 22
	H ₂ O		32.4	-44.4	242	1.5×10 ¹³	1, 3, 22
	H	0.9†				7.7×10 ¹²	22
(04°0) → (03°0, 01°0)	CO ₂	1.0	30.1	-171	264	3.0×10 ⁷	22
	N ₂ , O ₂ , CO	1.6				5.2×10 ⁷	22
	H ₂		29.6	-153	319	6.2×10 ⁸	22
	H ₂ O		29.2	-135	256	2.7×10 ⁸	22
(01°1) → (00°1)	CO ₂	1.0	38.5	-177	451	3.1×10 ¹¹	1, 15, 22
	N ₂ , O ₂ , CO	0.7				2.2×10 ¹¹	1, 15, 22
	H ₂		33.2	-83.0	345	2.5×10 ¹²	18, 22
	H ₂ O		31.1	-44.4	242	4.2×10 ¹²	1, 3, 22
	H	0.9†				2.3×10 ¹²	22

TABLE III a (continued)

REACTION	M	Q	A	B	C	k(1500°K)	SOURCE
(05 ¹ 0, 13 ¹ 0, 21 ¹ 0) → (05 ² 0, 13 ² 0)	CO ₂	1.0	38.4	- 88.9	226	1.1×10 ¹⁴	22
	N ₂ , O ₂ , CO	0.9				1.0×10 ¹⁴	22
	H ₂ O	0.33				3.7×10 ¹³	22
	H ₂	0.13				1.5×10 ¹³	22
	H	0.1				1.1×10 ¹²	22
(05 ³ 0, 13 ³ 0) → (05 ⁵ 0)	CO ₂	1.0	38.4	- 88.9	226	7.5×10 ¹³	22
	N ₂ , O ₂ , CO	0.9				6.8×10 ¹³	22
	H ₂ O	0.33				2.5×10 ¹³	22
	H ₂	0.13				9.8×10 ¹²	22
	H	0.1				7.5×10 ¹²	22
(05 ¹ 0, 13 ¹ 0, 21 ¹ 0) → (04 ² 0, 12 ² 0, 20 ² 0)	CO ₂	1.0	40.5	-177	451	2.3×10 ¹³	1, 15, 22
	N ₂ , O ₂ , CO	0.7				1.6×10 ¹³	1, 15, 22
	H ₂ O		33.2	- 44.4	242	3.4×10 ¹³	1, 3, 22
	H ₂		35.2	- 83.0	345	1.9×10 ¹³	18, 22
	H	0.9 [‡]				1.7×10 ¹³	22
(05 ¹ 0, 13 ¹ 0, 21 ¹ 0) → (04 ² 0, 12 ² 0)	CO ₂	1.0	40.4	-177	451	2.1×10 ¹³	1, 15, 22
	N ₂ , O ₂ , CO	0.7				1.5×10 ¹³	1, 15, 22
	H ₂ O		33.1	- 44.4	242	3.1×10 ¹³	1, 3, 22
	H ₂		35.1	- 83.0	345	1.7×10 ¹³	18, 22
	H	0.9 [‡]				1.5×10 ¹³	22
(05 ³ 0, 13 ³ 0) → (04 ² 0, 12 ² 0)	CO ₂	1.0	40.4	-177	451	2.1×10 ¹³	1, 15, 22
	N ₂ , O ₂ , CO	0.7				1.5×10 ¹³	1, 15, 22
	H ₂ O		33.1	- 44.4	242	3.1×10 ¹³	1, 3, 22
	H ₂		35.1	- 83.0	345	1.7×10 ¹³	18, 22
	H	0.9 [‡]				1.5×10 ¹³	22
(05 ¹ 0, 13 ³ 0) → (04 ⁴ 0)	CO ₂	1.0	39.9	-177	451	1.3×10 ¹³	1, 15, 22
	N ₂ , O ₂ , CO	0.7				9.1×10 ¹¹	1, 15, 22
	H ₂ O		32.6	- 44.4	242	1.9×10 ¹³	1, 3, 22
	H ₂		34.6	- 83.0	345	1.1×10 ¹³	18, 22
	H	0.9 [‡]				1.0×10 ¹³	22
(05 ⁵ 0) → (04 ⁴ 0)	CO ₂	1.0	39.9	-177	451	1.3×10 ¹³	1, 15, 22
	N ₂ , O ₂ , CO	0.7				9.1×10 ¹¹	1, 15, 22
	H ₂ O		32.6	- 44.4	242	1.9×10 ¹³	1, 3, 22
	H ₂		34.6	- 83.0	345	1.1×10 ¹³	18, 22
	H	0.9				1.0×10 ¹³	22
(05 ¹ 0, 13 ¹ 0, 21 ¹ 0) → (03 ¹ 0, 11 ¹ 0)	CO ₂	1.0	35.2	-137		1.2×10 ¹⁶	22
	N ₂ , O ₂ , CO	3.1				3.8×10 ¹³	22
	H ₂ O		27.9	- 44.0	242	1.7×10 ¹¹	22
	H ₂		40.6	-149	451	3.0×10 ¹³	22
	H	1.6 [‡]				4.8×10 ¹¹	22
(05 ¹ 0, 13 ¹ 0) → (03 ¹ 0)	CO ₂	1.0	34.1	-137		4.1×10 ⁹	22
	N ₂ , O ₂ , CO	3.1				1.3×10 ¹¹	22
	H ₂ O		26.8	- 44.0	242	6.2×10 ¹³	22
	H ₂		39.5	-149	451	1.0×10 ¹³	22
	H	1.6 [‡]				1.6×10 ¹¹	22

TABLE III b
INTERMOLECULAR V-V ENERGY TRANSFER RATES IN CO₂

REACTION	Z ₀ /S	A	B	C	k(1500°K)	SOURCE
(02°0, 10°0) + (00°0) → (01°1) + (01°1)	18	34.8	-88.0	233	3.5x10 ¹³	22
(02°0) + (00°0) → (01°1) + (01°1)	18	34.8	-88.0	233	3.5x10 ¹³	22
(03°1, 11°0) + (00°0) → (02°0, 10°0) + (01°1)	9.9	35.7	-88.2	233	8.2x10 ¹³	22
(03°1, 11°0) + (00°0) → (02°0) + (01°1)	12	35.2	-88.0	233	5.2x10 ¹³	22
(03°0) + (00°0) → (02°0) + (01°1)	12	35.2	-88.0	233	5.2x10 ¹³	22
(04°0, 12°0, 20°0) + (00°0) → (03°1, 11°0) + (01°1)	6	35.9	-88.0	233	1.0x10 ¹³	22
(04°0, 12°0, 20°0) + (00°0) → (02°0, 10°0) + (02°0, 10°0)	3	34.9	-89.0	234	3.8x10 ¹³	22
(04°0, 12°0) + (00°0) → (03°1, 11°0) + (01°1)	6	35.9	-88.0	233	1.0x10 ¹³	22
(04°0, 12°0) + (00°0) → (02°0) + (02°0, 10°0)	9	33.8	-89.0	234	1.3x10 ¹³	22
(04°0, 12°0) + (00°0) → (03°0) + (01°1)	9	35.5	-88.0	233	6.9x10 ¹³	22
(04°0) + (00°0) → (03°0) + (01°1)	9	35.5	-88.0	233	6.9x10 ¹³	22
(01°1) + (00°0) → (00°1) + (01°1)	36.9	34.1	-87.7	230	1.8x10 ¹³	22
(03°1, 11°0) + (01°1) → (02°0, 10°0) + (02°0, 10°0)	4.5	36.2	-88.0	232	1.4x10 ¹³	22
(03°1, 11°0) + (01°1) → (02°0, 10°0) + (02°0, 10°0)	6.4.5	35.7	-88.0	233	4.3x10 ¹³	22
(03°1, 11°0) + (01°1) → (02°0) + (02°0)	6	35.9	-88.0	233	1.0x10 ¹³	22
(03°0) + (01°1) → (02°0) + (02°0)	6	35.9	-88.0	233	1.0x10 ¹³	22
(03°0) + (01°1) → (02°0) + (02°0, 10°0)	6	35.9	-88.0	233	1.0x10 ¹³	22
(04°0, 12°0, 20°0) + (01°1) → (03°1, 11°0) + (02°0)	3	36.6	-88.0	233	2.0x10 ¹³	22
(04°0, 12°0, 20°0) + (01°1) → (03°1, 11°0) + (02°0, 10°0)	3.3	36.7	-88.2	233	2.3x10 ¹³	22
(04°0, 12°0) + (01°1) → (03°1, 11°0) + (02°0)	3.9	36.6	-88.0	233	2.1x10 ¹³	22
(04°0, 12°0) + (01°1) → (03°1, 11°0) + (02°0, 10°0)	3	36.6	-88.0	233	2.0x10 ¹³	22
(04°0) + (01°1) → (03°0) + (02°0)	4.5	36.2	-88.0	233	1.4x10 ¹³	22
(04°0) + (01°1) → (03°0) + (02°0, 10°0)	4.5	36.2	-88.0	233	1.4x10 ¹³	22
(01°1) + (01°1) → (00°1) + (02°0)	18	34.8	-88.0	233	3.5x10 ¹³	22
(01°1) + (01°1) → (00°1) + (02°0, 10°0)	18	34.8	-88.0	233	3.5x10 ¹³	22
(04°0, 12°0, 20°0) + (02°0, 10°0) → 2(03°1, 11°0)	1.5	37.3	-88.0	233	4.0x10 ¹³	22
(04°0, 12°0) + (02°0, 10°0) → 2(03°1, 11°0)	1.5	37.3	-88.0	233	4.0x10 ¹³	22
(04°0, 12°0) + (02°0, 10°0) → (03°0) + (03°1, 11°0)	2.25	36.9	-88.0	233	2.8x10 ¹³	22
(04°0, 12°0) + (02°0, 10°0) → (02°0) + (04°0, 12°0, 20°0)	3.0	34.9	-89.0	234	3.8x10 ¹³	22
(04°0) + (02°0, 10°0) → (03°0) + (03°1, 11°0)	2.25	36.9	-88.0	234	2.8x10 ¹³	22
(01°1) + (02°0, 10°0) → (00°1) + (03°1, 11°0)	9	35.5	-88.0	233	6.9x10 ¹³	22
(04°0, 12°0, 20°0) + (02°0) → (03°1, 11°0) + (03°0)	2	37.0	-88.0	233	3.0x10 ¹³	22
(04°0, 12°0, 20°0) + (02°0) → (03°1, 11°0) + (03°1, 11°0)	2	37.0	-88.0	233	3.0x10 ¹³	22
(04°0, 12°0) + (02°0) → (03°1, 11°0) + (03°1, 11°0)	2	37.0	-88.0	233	3.0x10 ¹³	22
(04°0, 12°0) + (02°0) → (03°1, 11°0) + (03°0)	2.3	37.5	-88.0	233	5.0x10 ¹³	22
(04°0, 12°0) + (02°0) → (03°0) + (03°0)	3	36.6	-88.0	233	2.0x10 ¹³	22
(04°0) + (02°0) → (03°0) + (03°0)	3	36.6	-88.0	233	2.0x10 ¹³	22
(04°0) + (02°0) → (03°0) + (03°1, 11°0)	3	36.6	-88.0	233	2.0x10 ¹³	22
(01°1) + (02°0) → (00°1) + (03°0)	12	35.2	-88.0	233	5.2x10 ¹³	22
(01°1) + (02°0) → (00°1) + (03°1, 11°0)	12	35.2	-88.0	233	5.2x10 ¹³	22
(01°1) + (03°1, 11°0) → (00°1) + (04°0, 12°0, 20°0)	6	35.9	-88.0	233	1.0x10 ¹³	22
(01°1) + (03°1, 11°0) → (00°1) + (04°0, 12°0)	6	35.9	-88.0	233	1.0x10 ¹³	22
(01°1) + (03°0) → (00°1) + (02°0)	12	35.2	-88.0	233	5.2x10 ¹³	22

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TABLE III b (continued)

REACTION	Z ₀ /S	A	B	C	$\lambda(1500^\circ\text{K})$	SOURCE
$(05^0, 13^1, 21^1) + (00^0) \rightarrow (04^0, 12^0, 20^0) + (01^1)$	4	36.3	- 88.0	232	1.5×10^{13}	22
$(05^0, 13^1, 21^1) + (00^0) \rightarrow (04^0, 12^0) + (01^1)$	4.5	36.2	- 88.0	233	1.4×10^{14}	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0, 20^0) + (02^0)$	2.0	37.6	- 88.0	233	3.0×10^{13}	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0, 20^0) + (02^0, 10^0)$	2.0	37.5	- 88.0	233	3.0×10^{13}	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0) + (01^1)$	2.25	36.9	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	2.25	36.9	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0, 20^0) + (03^0)$	1.33	37.4	- 88.0	233	4.7×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0, 20^0) + (03^0, 11^1)$	1.33	37.4	- 88.0	233	4.7×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0)$	1.5	37.3	- 88.0	233	4.3×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.5, 3	37.5	- 88.0	233	5.2×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0, 10^0) \rightarrow (04^0, 12^0, 20^0) + (03^0, 11^1)$	1.3	37.8	- 88.0	233	7.1×10^{13}	22
$(05^0, 13^1, 21^1) + (02^0, 10^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.13	37.6	- 88.0	233	5.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow 2(04^0, 12^0, 20^0)$	0.67	38.1	- 88.0	233	9.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0, 20^0) + (04^0, 12^0)$	0.67	38.1	- 88.0	233	9.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0) \rightarrow (04^0, 12^0, 20^0) + (04^0)$	1.0	37.7	- 88.0	233	6.4×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0) \rightarrow 2(04^0, 12^0)$	1.13	37.6	- 88.0	233	5.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (01^1)$	4.5	36.2	- 88.0	233	1.4×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (01^1)$	7.2	35.7	- 88.0	233	3.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	2.25	36.9	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	3.6	36.4	- 88.0	233	1.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	2.25	36.9	- 88.0	233	2.8×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	3.6	36.4	- 88.0	233	1.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.13	37.6	- 88.0	233	5.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	3.6	36.4	- 88.0	233	1.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.5	37.3	- 88.0	233	4.3×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.5, 3	37.5	- 88.0	233	5.3×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	2.4	36.8	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	2.4	36.8	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	7.2	35.7	- 88.0	233	8.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	3.6	36.4	- 88.0	233	1.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	3.6	36.4	- 88.0	233	1.7×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	2.4	36.8	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	2.4	36.8	- 88.0	233	2.6×10^{13}	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.8	37.1	- 88.0	233	3.4×10^{13}	22

TABLE III c
SCRAMBLING ‡ REACTIONS IN CO₂

REACTION	Z ₀	A	B	C	k (1500°K)	SOURCE
(02°0, 10°0) + (01°0) → (01°0) + (02°0)	9	35.5	-88.0	233	6.9 × 10 ¹²	22
(03°0, 11°0) + (02°0, 10°0) → (02°0) + (03°0, 11°0)	4	36.3	-88.0	233	1.5 × 10 ¹³	22
(03°0, 11°0) + (02°0) → (02°0) + (03°0)	4	36.3	-88.0	233	1.5 × 10 ¹³	22
(03°0, 11°0) + (02°0) → (02°0, 10°0) + (03°0)	3	36.6	-88.0	233	2.0 × 10 ¹³	22
(03°0, 11°0) + (02°0) → (02°0, 10°0) + (03°0, 11°0)	3	36.6	-88.0	233	2.0 × 10 ¹³	22
(04°0, 12°0, 20°0) + (03°0, 11°0) → (03°0, 11°0) + (04°0, 12°0)	1	37.7	-88.0	233	6.0 × 10 ¹³	22
(04°0, 12°0) + (03°0, 11°0) → (03°0) + (04°0, 12°0)	1.5	37.3	-88.0	233	4.0 × 10 ¹³	22
(04°0, 12°0) + (03°0, 11°0) → (03°0) + (04°0, 12°0, 10°0)	1.5	37.3	-88.0	233	4.0 × 10 ¹³	22
(04°0, 12°0, 20°0) + (03°0) → (03°0, 11°0) + (04°0)	1.5	37.3	-88.0	233	4.0 × 10 ¹³	22
(04°0, 12°0) + (03°0) → (03°0, 11°0) + (04°0)	1.5	37.3	-88.0	233	4.0 × 10 ¹³	22
(04°0, 12°0) + (03°0) → (03°0) + (04°0)	2.25	36.9	-88.0	233	2.8 × 10 ¹³	22
(04°0, 12°0) + (03°0) → (03°0, 11°0) + (04°0, 12°0)	1.5	37.3	-88.0	233	4.0 × 10 ¹³	22

‡ Reactions involving changes only in the quantum no. ℓ .

TABLE III d
V-T AND INTRAMOLECULAR V-V ENERGY EXCHANGES IN SPECIES OTHER THAN CO₂

REACTION	M	σ	A	B	C	$k(1500^\circ K)$	SOURCE
$H_2O(010) \rightarrow H_2O(000)$	H ₂ O	1.0	52.8	-363	1462	1.0×10^{14}	33-37
	N ₂ , O ₂ , CO		48.5	-243	573	4.3×10^{13}	37
	CO ₂		50.8	-300	813	2.3×10^{13}	37
	H ₂		35.2	-14.0		6.0×10^{14}	37*
	H	1.4 $\frac{1}{2}$				8.4×10^{14}	37*
$H_2O(020) \rightarrow H_2O(010)$	H ₂ O		53.5	-363	1452	2.0×10^{14}	33-37
	N ₂ , O ₂ , CO		49.2	-243	558	9.8×10^{13}	37
	CO ₂		51.5	-300	813	4.6×10^{13}	37
	H ₂		35.2	-14.0		6.0×10^{14}	37*
	H	1.4 $\frac{1}{2}$				8.4×10^{14}	37*
$H_2O(001) \rightarrow H_2O(000)$	H ₂ O	1.0	55.1	-522	1599	5.5×10^{14}	37
	N ₂ , O ₂ , CO		53.9	-451	1131	1.2×10^{15}	37
	CO ₂		55.8	-512	1354	2.1×10^9	37
	H ₂		46.5	-273	1059	2.3×10^{13}	37
	H		44.7	-224	939	1.0×10^{14}	37
$H_2O(100) \rightarrow H_2O(000)$	H ₂ C	1.0	58.6	-541	2084	6.4×10^{11}	37
	N ₂ , O ₂ , CO		55.3	-435	1079	1.3×10^{11}	37
	CO ₂		57.7	-503	1331	2.4×10^{10}	37
	H ₂ O		58.6	-541	2084	6.4×10^{11}	37
	H ₂		47.2	-229	321	3.4×10^{14}	37
	H		46.6	-218	920	5.4×10^{14}	37
$H_2O(001) + H_2O(100)$	H ₂ O	1.0	36.9	-88.7	250	3.1×10^{13}	22*
	N ₂	1.4				4.3×10^{13}	22
	H ₂	0.6				1.9×10^{13}	22
	CO ₂	1.7				5.3×10^{17}	22
	H	0.5				1.5×10^{13}	22
$N_2(1) \rightarrow N_2(0)$	H	2.1 $\frac{1}{2}$				1.8×10^{11}	22
	N ₂ , O ₂ , CO	1.0	42.2	-292		1.8×10^7	1, 22
	CO ₂	0.14				2.5×10^6	1, 22
	H ₂ O		38.3	-124		2.5×10^{11}	1
	H ₂		32.7	-90.2		6.0×10^{10}	1, 4
$N_2(1) + N_2(1)$	N ₂ , O ₂ , CO	1.0	42.9	-292		3.6×10^7	1, 22
	CO ₂	0.14				5.0×10^6	1, 22
	H ₂ O		39.0	-124		1.7×10^{13}	1, 22
	H ₂		33.4	-90.2		1.2×10^{11}	1, 4, 22
	H $\frac{1}{2}$	3.1				3.6×10^{11}	22
$O_2(1) \rightarrow O_2(0)$	N ₂ , O ₂ , CO	1.0	36.6	-158		7.9×10^9	1, 22
	CO ₂	0.3				2.4×10^9	1, 22
	H ₂ O		42.6	-124		6.2×10^{13}	1, 43
	H ₂		33.0	-56.6		6.4×10^{11}	88
	H	1.7				1.1×10^{13}	22

TABLE III d (continued)
V-T AND INTRAMOLECULAR V-V ENERGY EXCHANGES IN SPECIES OTHER THAN CO₂

REACTION	M	Q	A	B	C	k(1500°K)	SOURCE
O ₂ (2) + O ₂ (1)	N ₂ , C ₂ , CO	1.0	37.3	-158		1.6×10 ¹⁰	1,22
	CO ₂	0.3				4.8×10 ⁹	1,22
	H ₂ O		43.3	-124		1.3×10 ¹⁴	1,22
	H ₂		33.7	-66.6		1.3×10 ¹²	83,22
	H	1.7				2.2×10 ¹⁷	22
CO(1) + CO(0)	CO	1.0	41.2	-244		4.3×10 ⁸	24-27
	N ₂ , O ₂		42.1	-289		3.1×10 ⁷	27,22
	H ₂		37.9	-176	383	1.1×10 ¹¹	27
	H ₂ O		24.3	+146	-1246	9.5×10 ¹¹	40
	H		44.4	-164		1.1×10 ¹³	32
CO(2) + CO(1)	CO	1.0	41.9	-244		8.7×10 ⁸	24-27,22
	N ₂ , O ₂		43.2	-289		6.3×10 ⁷	27,22
	H ₂		38.6	-176	383	2.2×10 ¹¹	27,22
	H ₂ O		25.0	+146	-1246	1.9×10 ¹³	40,22
	H		45.1	-164		2.3×10 ¹³	32,22
OH(1) + OH(0)	OH		42.0	-243	762	3.5×10 ¹¹	56
	N ₂	1.0	39.3	-210		1.3×10 ⁹	37
	O ₂	3.0					37
	CO	1.0					
	CO ₂	7.0					
	H ₂ O	60					
H ₂ (1) + H ₂ (0)	H ₂	1.0	40.4	-227	529	5.2×10 ¹¹	57,58,59
	N ₂ , O ₂ , CO	0.08				4.2×10 ¹¹	22
	CO ₂	0.07				3.6×10 ¹⁰	22
	H	2.2				1.1×10 ¹²	22
	H ₂ O	0.23				1.2×10 ¹¹	22

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$\text{CO}(1) + \text{N}_2(0) \rightarrow \text{CO}(0) + \text{N}_2(1)$	9	32.6				
$\text{CO}_2(00^0 1) + \text{CO}(0) \rightarrow \text{CO}_2(00^0 0) + \text{CO}(1)$	9	28.7	0.0	- 153	4.5×10^{11}	14
$\text{CO}_2(01^1 1) + \text{CO}(0) \rightarrow \text{CO}_2(01^1 0) + \text{CO}(1)$	9	28.7	0.0	- 153	4.5×10^{11}	14, 22
$\text{H}_2(1) + \text{H}_2\text{O}(000) \rightarrow \text{H}_2(0) + \text{H}_2\text{O}(001)$	9	35.6	- 67.0	62.1	1.4×10^{13}	22
$\text{H}_2(1) + \text{H}_2\text{O}(000) \rightarrow \text{H}_2(0) + \text{H}_2\text{O}(100)$	9	39.1	-138	390	1.7×10^{13}	22
$\text{H}_2(1) + \text{OH}(0) \rightarrow \text{H}_2(0) + \text{OH}(1)$	9	43.1	-232	839	3.2×10^{12}	22
$\text{H}_2\text{O}(001) + \text{OH}(0) \rightarrow \text{H}_2\text{O}(000) + \text{OH}(1)$	9	36.5	- 62.5	16.9	3.4×10^{13}	22
$\text{H}_2\text{O}(100) + \text{OH}(0) \rightarrow \text{H}_2\text{O}(000) + \text{OH}(1)$	9	36.6	- 62.5	17.0	3.7×10^{13}	22

Notations:

† Measured Relative to k_{H_2} .

• Collision Frequency

•• Molecular wt. of collision partner (H_2O) set to $1/\sigma^2 = 3.96$ in equation¹ for P_{10} to account for R-V interaction. Energy exchanged by single quantum steps.

TABLE IVa.

ALTERNATE TABLE OF RESONANT INTERMOLECULAR V-V
ENERGY EXCHANGE RATES AMONG CO₂ MOLECULES

REACTION	Z ₀ /S	A	B	C	k(1500°K)	SOURCE
(m2p) + (000) → (m1p) + (010)	18	34.8	-88.0	233	3.5×10 ¹³	22
(m3p) + (000) → (m2p) + (010)	12	35.2	-88.0	233	5.2×10 ¹³	22
(m4p) + (000) → (m3p) + (010)	9	35.5	-88.0	233	6.9×10 ¹³	22
(m5p) + (000) → (m4p) + (010)	7.2	35.7	-88.0	233	8.8×10 ¹³	22
(m6p) + (000) → (m5p) + (010)	6	35.9	-88.0	233	1.1×10 ¹³	22
(m3p) + (010) → (m2p) + (020)	6	35.9	-88.0	233	1.1×10 ¹³	22
(m4p) + (010) → (m3p) + (020)	4.5	36.2	-88.0	233	1.4×10 ¹³	22
(m5p) + (010) → (m4p) + (020)	3.6	36.4	-88.0	233	1.8×10 ¹³	22
(m6p) + (010) → (m5p) + (020)	3	36.6	-88.0	233	2.2×10 ¹³	22
(m4p) + (020) → (m3p) + (030)	3	36.6	-88.0	233	2.2×10 ¹³	22
(m5p) + (020) → (m4p) + (030)	2.4	36.8	-88.0	233	2.6×10 ¹³	22
(m6p) + (020) → (m5p) + (030)	2	37.0	-88.0	233	3.2×10 ¹³	22

TABLE IVb.
RESONANT INTERMOLECULAR V-V ENERGY EXCHANGE RATES BETWEEN
SYMMETRIC STRETCHING MODES OF CO₂ MOLECULES

REACTION	Z ₀ /S	A	B	C	k(1500°K)	SOURCE
(l _{np}) + (000) → (0 _{np}) + (100)	9	34.2	-88.0	233	1.9×10 ¹³	22
(l _{np}) + (010) → (0 _{np}) + (110)	9	34.2	-88.0	233	1.9×10 ¹³	22
(l _{np}) + (020) → (0 _{np}) + (120)	9	34.2	-88.0	233	1.9×10 ¹³	22
(l _{np}) + (100) → (0 _{np}) + (200)	4.5	34.5	-88.0	233	3.8×10 ¹³	22
(l _{np}) + (030) → (0 _{np}) + (130)	9	34.2	-88.0	233	1.9×10 ¹³	22
(l _{np}) + (110) → (0 _{np}) + (210)	4.5	34.9	-88.0	233	3.8×10 ¹³	22
(m _{nl}) + (000) → (m _{n0}) + (001)	9	32.5	-88.0	233	3.5×10 ¹¹	22
(m _{nl}) + (010) → (m _{n0}) + (011)	9	32.5	-88.0	233	3.5×10 ¹¹	22
(m _{nl}) + (020) → (m _{n0}) + (021)	9	32.5	-88.0	233	3.5×10 ¹¹	22
(m _{nl}) + (100) → (m _{n0}) + (101)	9	32.5	-88.0	233	3.5×10 ¹¹	22
(m _{nl}) + (030) → (m _{n0}) + (031)	9	32.5	-88.0	233	3.5×10 ¹¹	22

TABLE V
EINSTEIN COEFFICIENTS FOR SPONTANEOUS
EMISSION

REACTION	A(sec ⁻¹)	LIFETIME(ms)	Wavelength (microns)	ω (cm ⁻¹)	Source
CO ₂ (01 ¹ 0) → CO ₂ (00 ⁰ 0)	2.98	335	14.98	667.4	44
CO ₂ (00 ⁰ 1) → CO ₂ (00 ⁰ 0)	424.6	2.4	4.20	2349.2	45
CO ₂ (02 ² 1) → CO ₂ (00 ⁰ 0)	11.4	88	2.75	3634.6	49
CO ₂ (10 ⁰ 1) → CO ₂ (00 ⁰ 0)	17.9	56	2.68	3737.4	49
CO ₂ (03 ¹ 0) → CO ₂ (00 ⁰ 0)	.0022	460829	5.17	1932.5	47
CO ₂ (11 ¹ 0) → CO ₂ (00 ⁰ 0)	.0166	60147	4.81	2076.9	47
CO(2) → CO(0)	0.9	1098	2.35	4260	46,48
CO(1) → CO(0)	33.4	29.9	4.67	2143	46,48
CO(2) → CO(1)	62.0	16.1	4.73	2116	46,48
H ₂ O(010) → H ₂ O(000)	22.1	45.2	6.27	1595.0	46,50
H ₂ O(001) → H ₂ O(000)	74.7	13.4	2.66	3755.8	51
H ₂ O(100) → H ₂ O(000)	4.0	250	2.74	3651.2	52
OH(1) → OH(0)	3.3	300	2.71	3682	20

9. FIGURES

1. Review of experimentally derived rate constants for the deactivation of CO_2 ($01^1 0$) by various collision partners.
2. Review of experimentally derived rate constants for the deactivation of CO_2 ($00^0 1$) by various collision partners.
3. Review of deactivation rates derived from theory²² and experiment for the process CO_2 ($00^0 1$) + $\text{CO}_2 \rightarrow \text{CO}_2$ ($mn^l p$) + CO_2 .
4. Review of experimentally derived rate constants for the V-V energy transfers between CO_2 ($00^0 1$) and N_2 (0) or CO (0).
5. Review of experimental data for the self deactivation of H_2O (010).
6. Review of experimental results for the deactivation of N_2 (1) by various collision partners.
7. Review of experimental results for the deactivation of O_2 (1) by O_2 , H_2 , and H_2O .
8. Review of experimental results for the deactivation of CO (1) by various collision partners.
9. Review of experimental results for the V-V transfers of energy between some diatomic molecules.
10. Review of experimental results for the deactivation of H_2 (1) by H_2 .

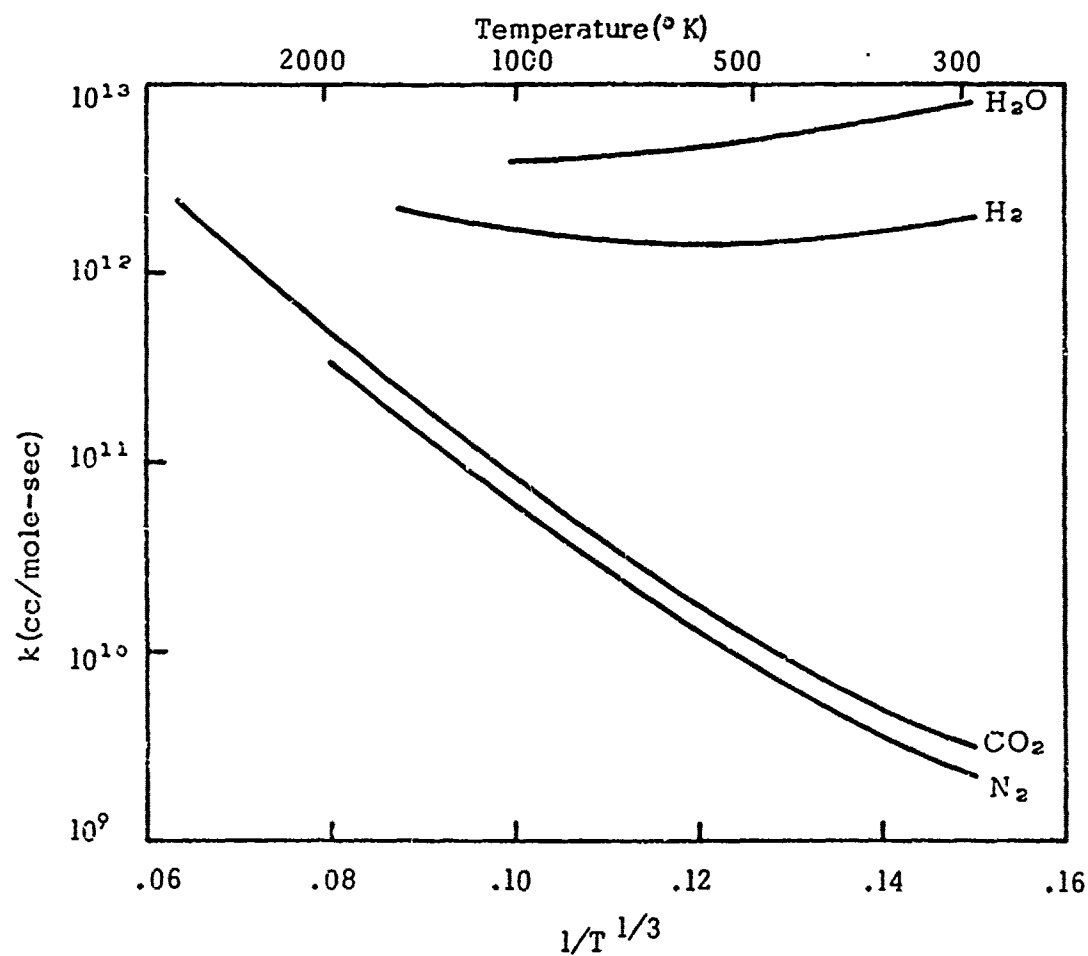
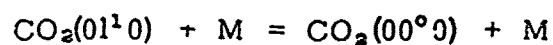


Figure 1 Review of experimentally derived rate constants for the deactivation of $CO_2(01^1 0)$ by various collision partners



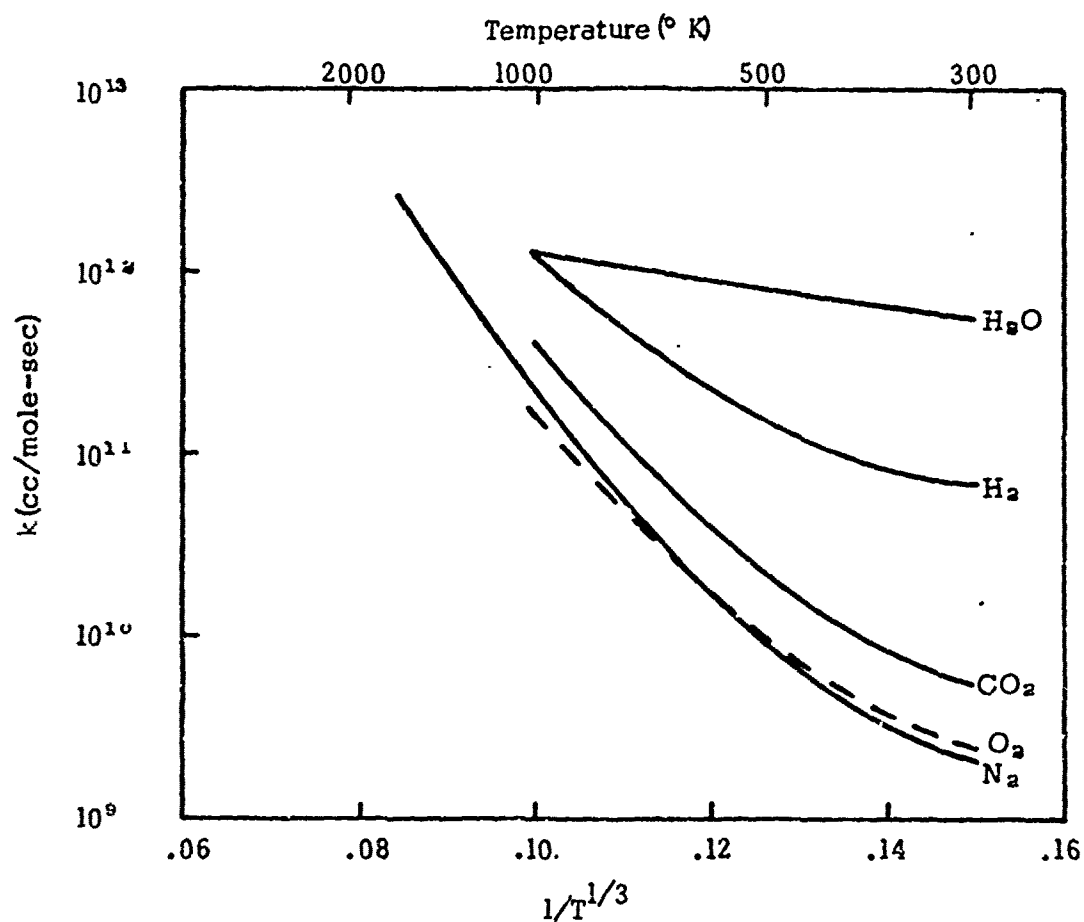


Figure 2 Review of experimentally derived rate constants for the deactivation of $\text{CO}_2(00^u1)$ by various collision partners.



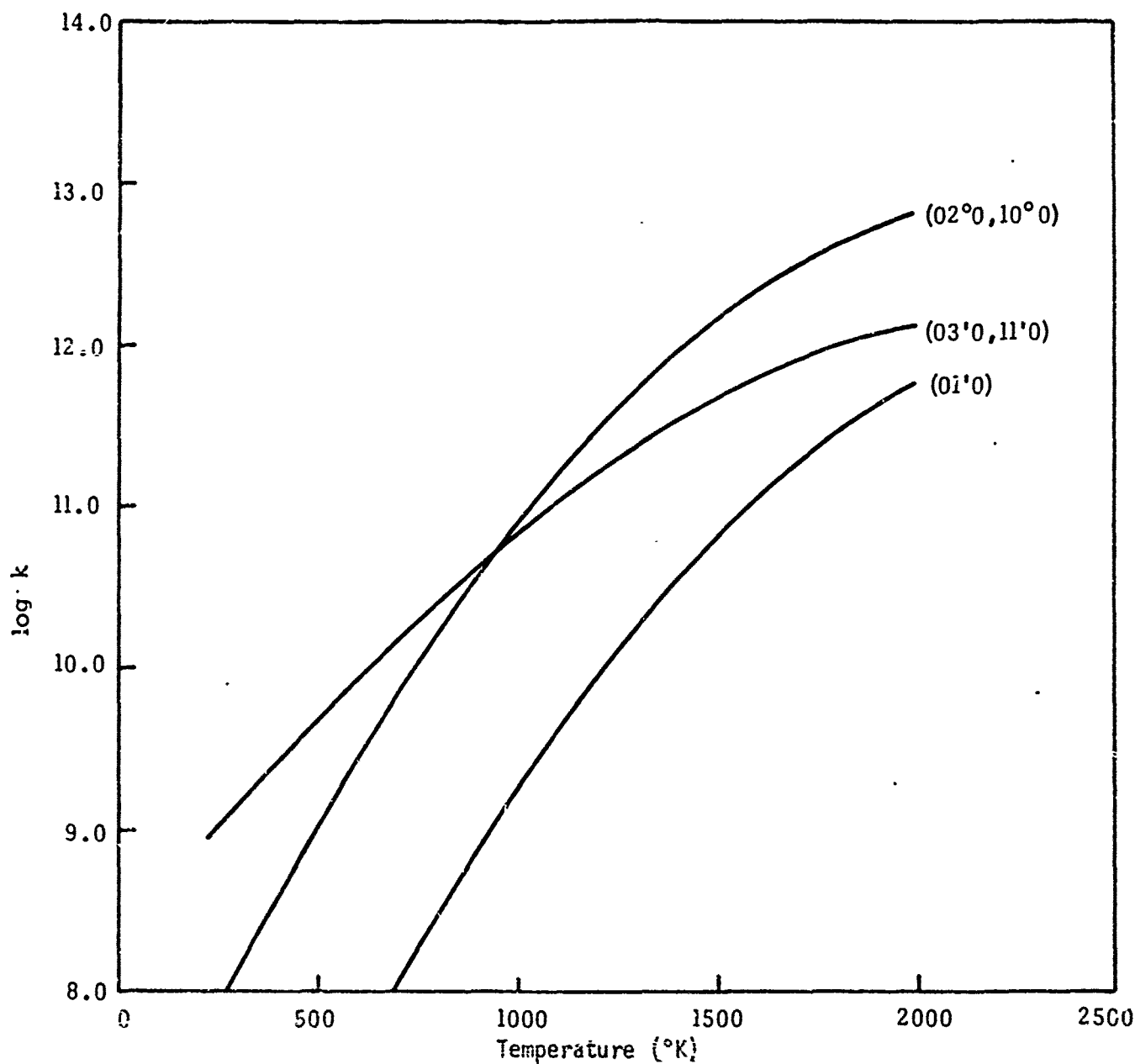
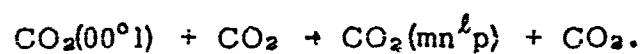


Figure 3 Review of deactivation rates derived from theory²² and experiment for the process



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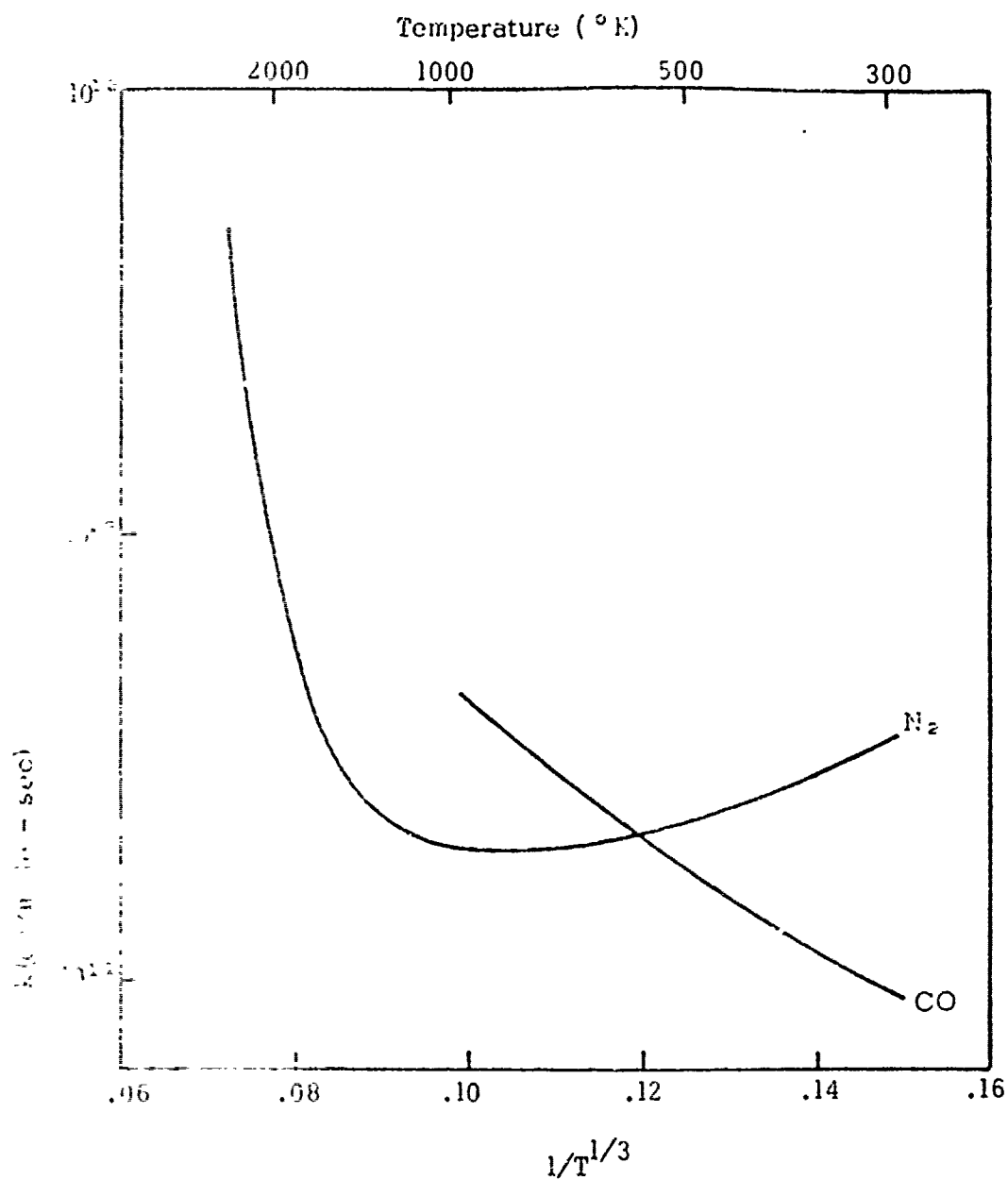
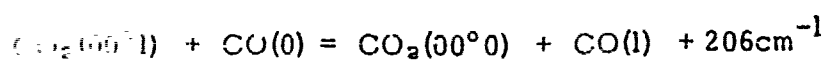
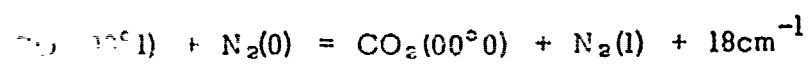


Figure 1. Review of experimentally derived rate constants for the
energy transfers between CO₂(00°1) and N₂(0) or CO(0)



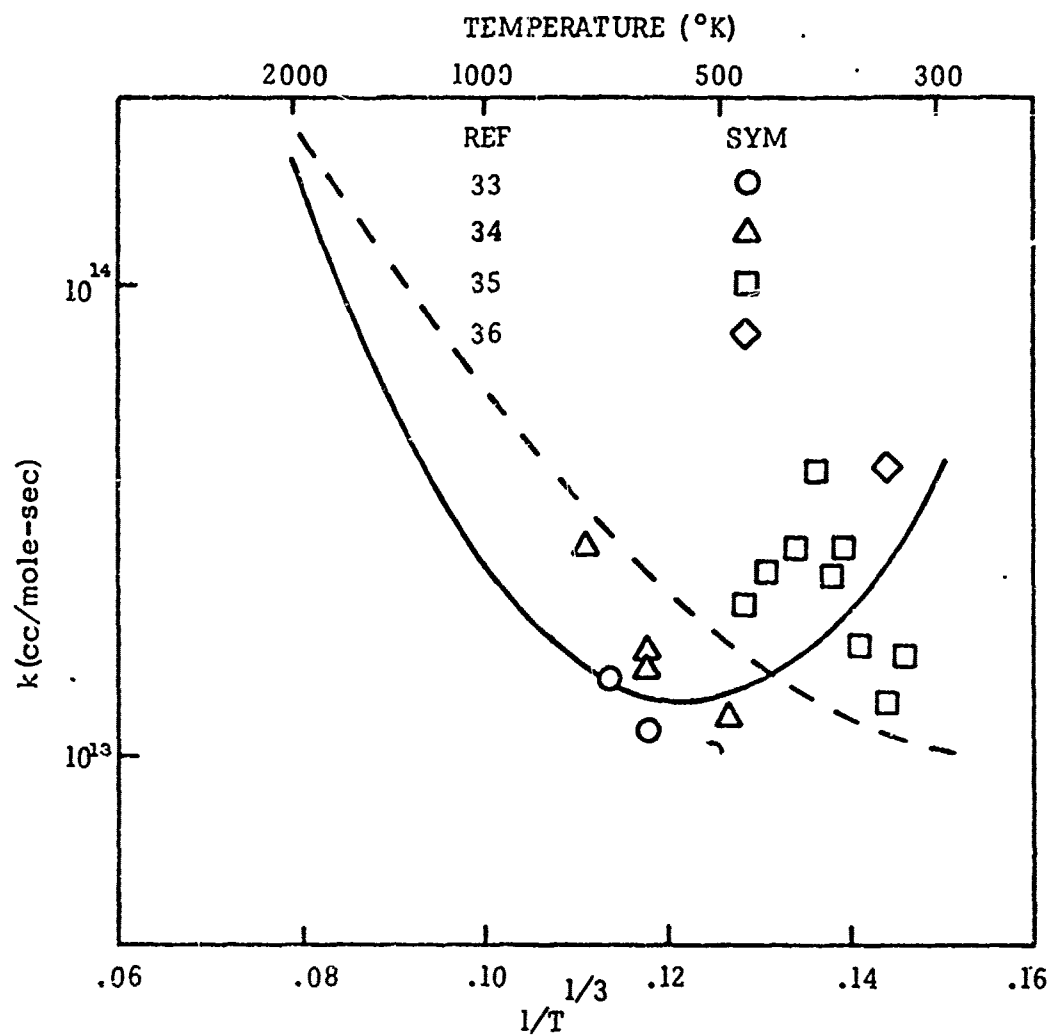


Figure 5 Review of experimental data for the self deactivation of $H_2O(010)$.



Shin V-T exchange (37) ——— ; Shin V-R exchange (70) - - - - -.

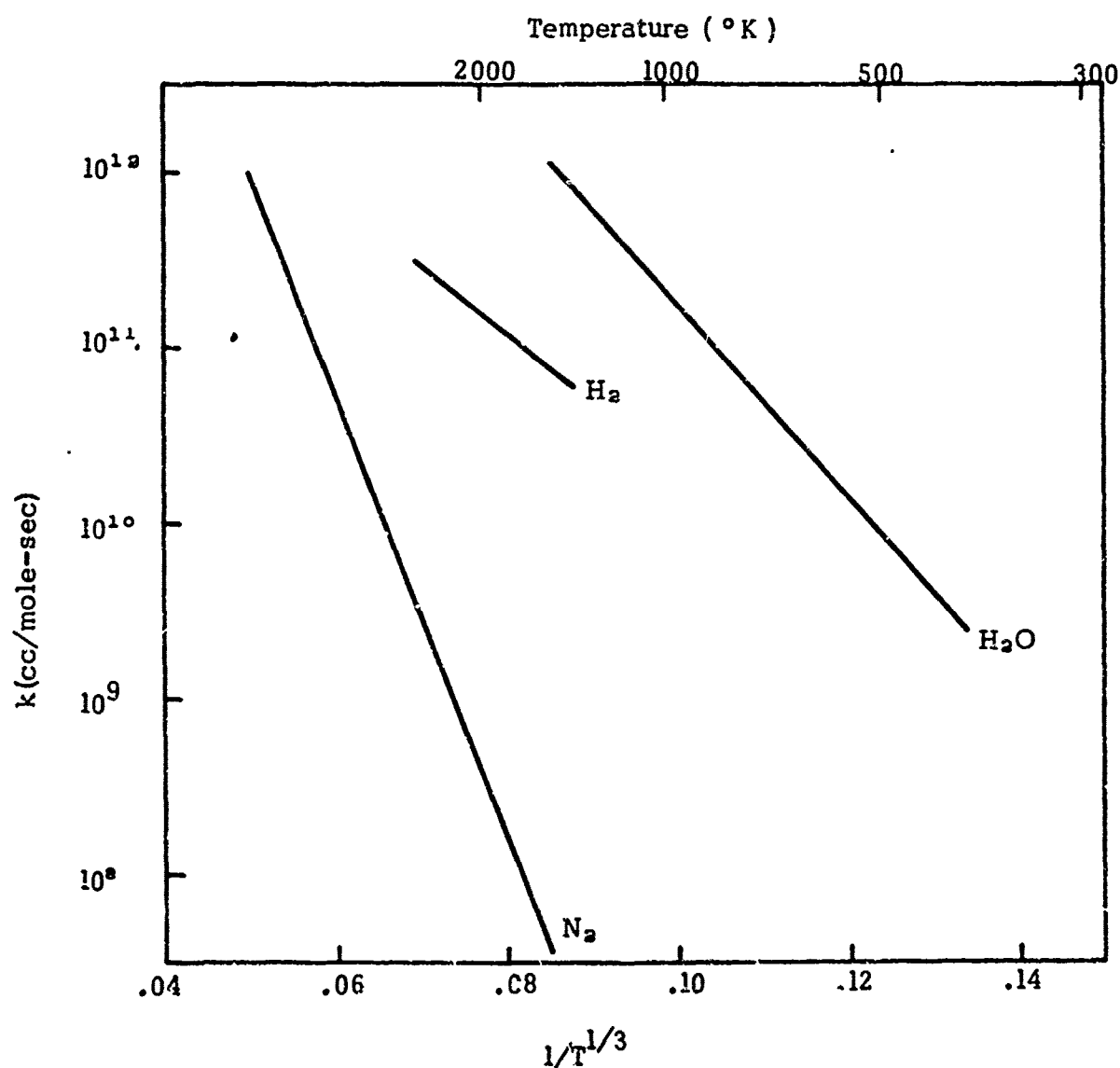


Figure 6 Review of experimental results for the deactivation of $\text{N}_2(l)$ by various collision partners



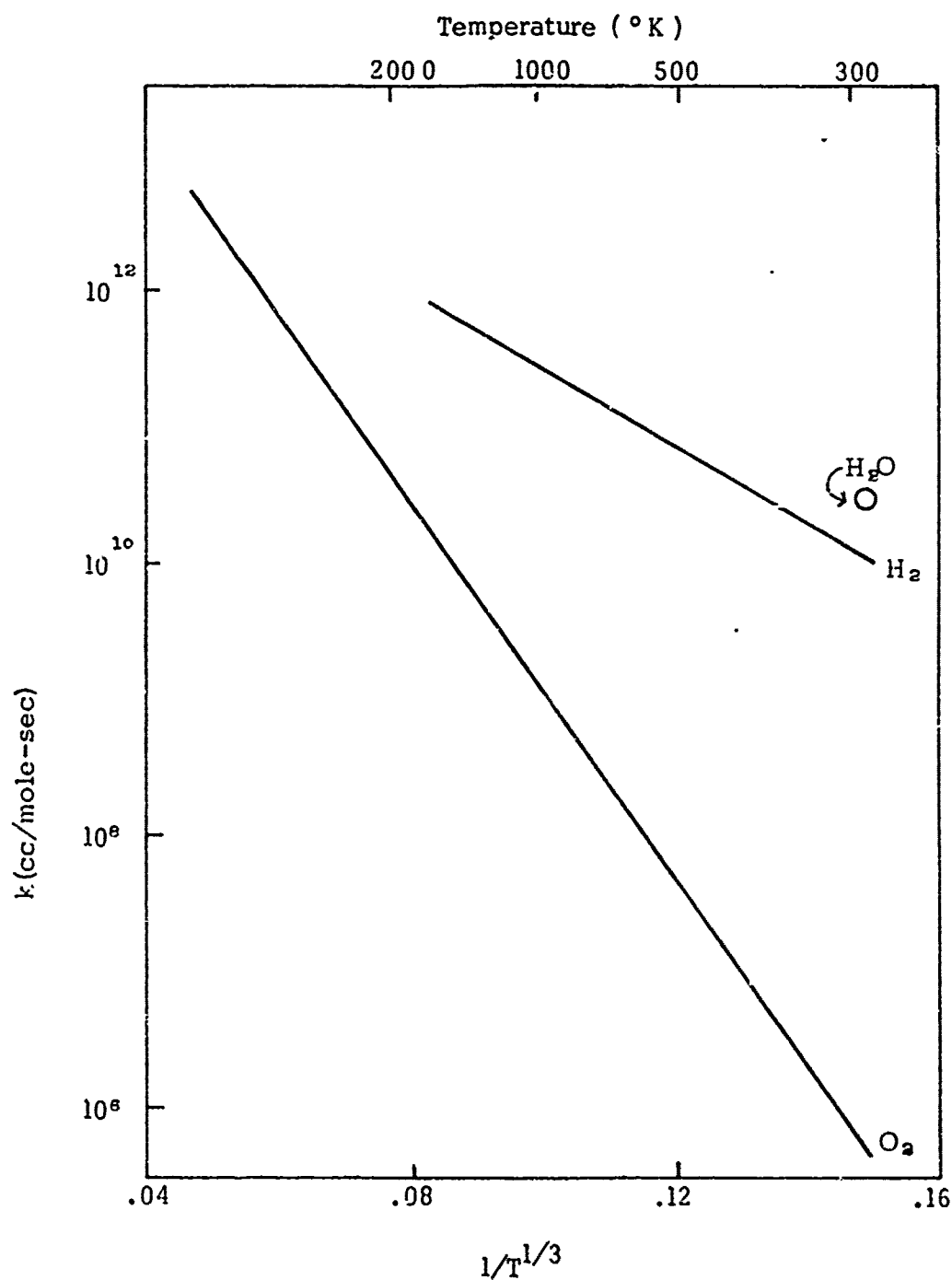


Figure 7 Review of experimental results for the deactivation of $O_2(l)$ by O_2 , H_2 , and H_2O .



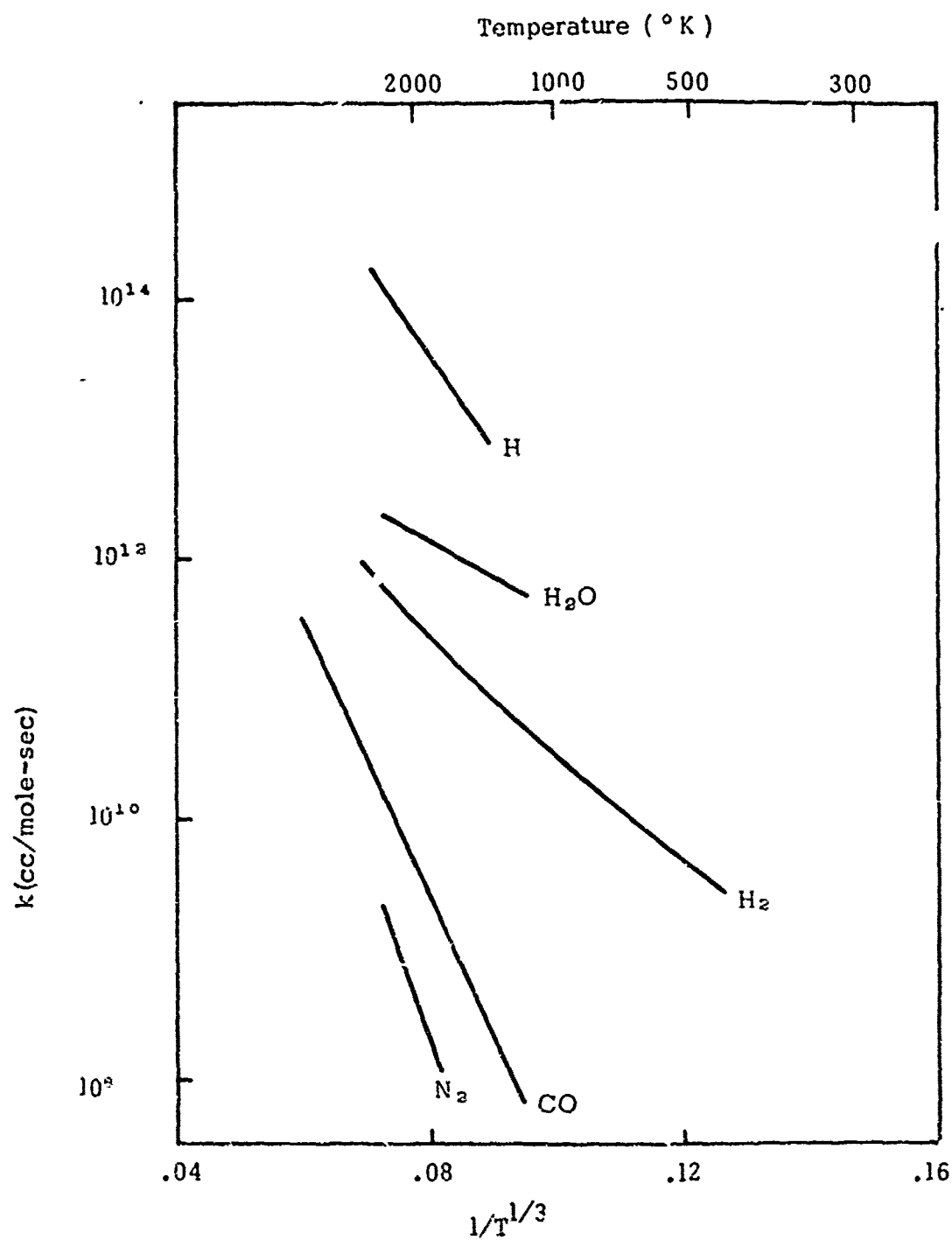


Figure 8 Review of experimental results for the deactivation of CO(l) by various collision partners $\text{CO(l)} + \text{M} \rightarrow \text{CO(0)} + \text{M}$.

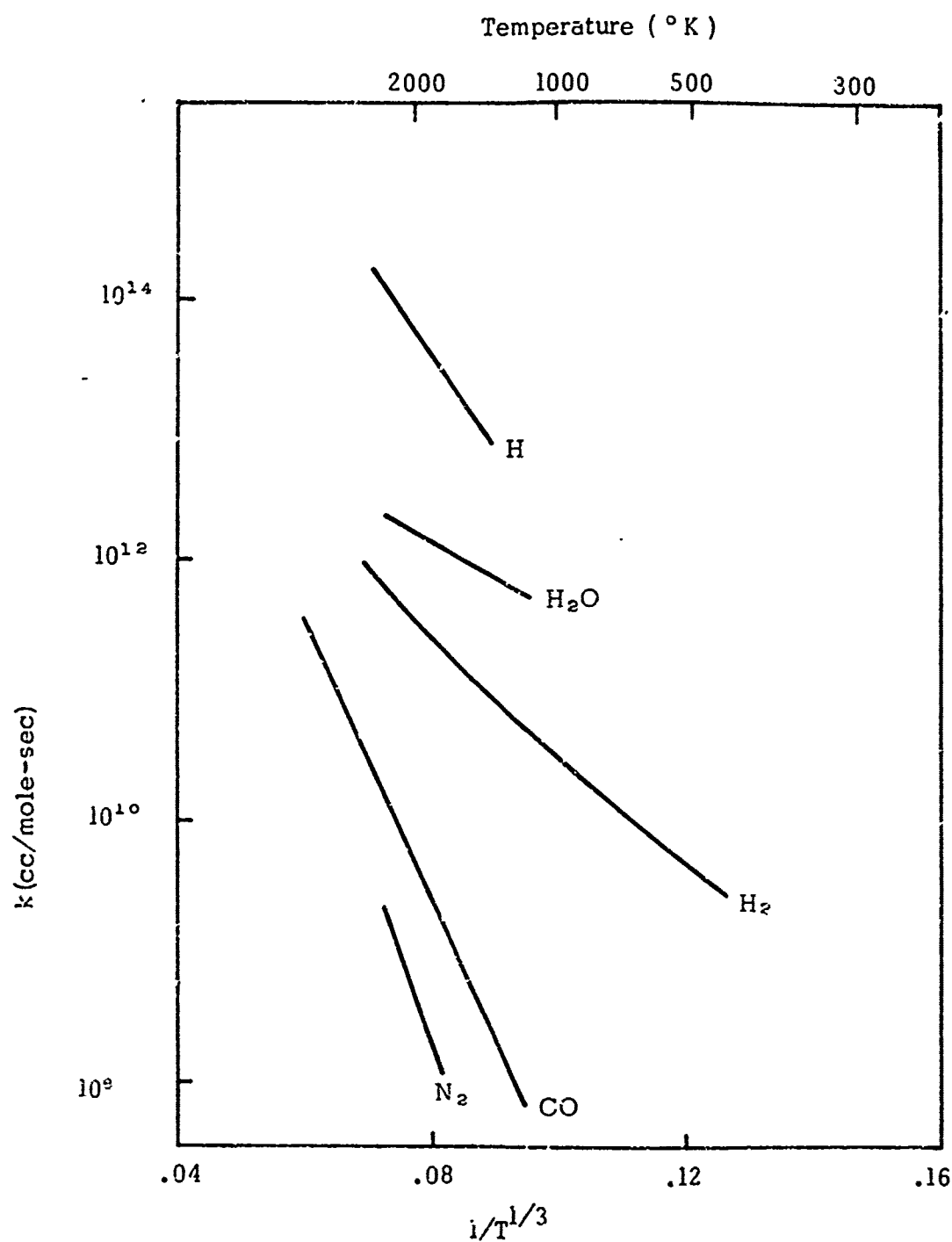


Figure 5 Review of experimental results for the deactivation of $CO(l)$ by various collision partners $CO(l) + M \rightarrow CO(0) + M$.

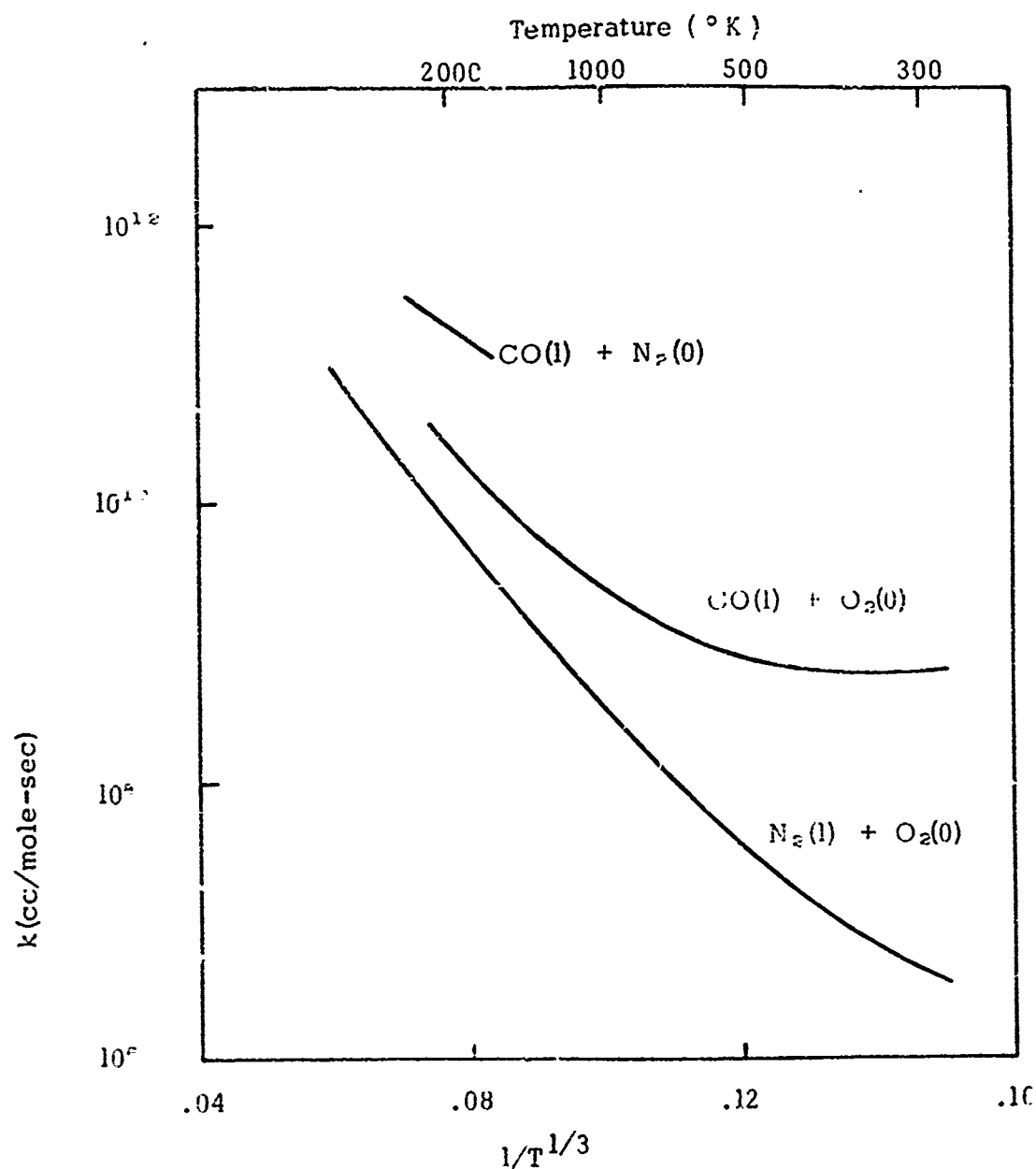
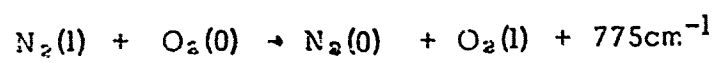
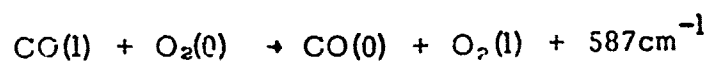
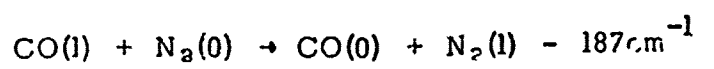


Figure 9 Review of experimental results for the V-V transfers of energy between some diatomic molecules.



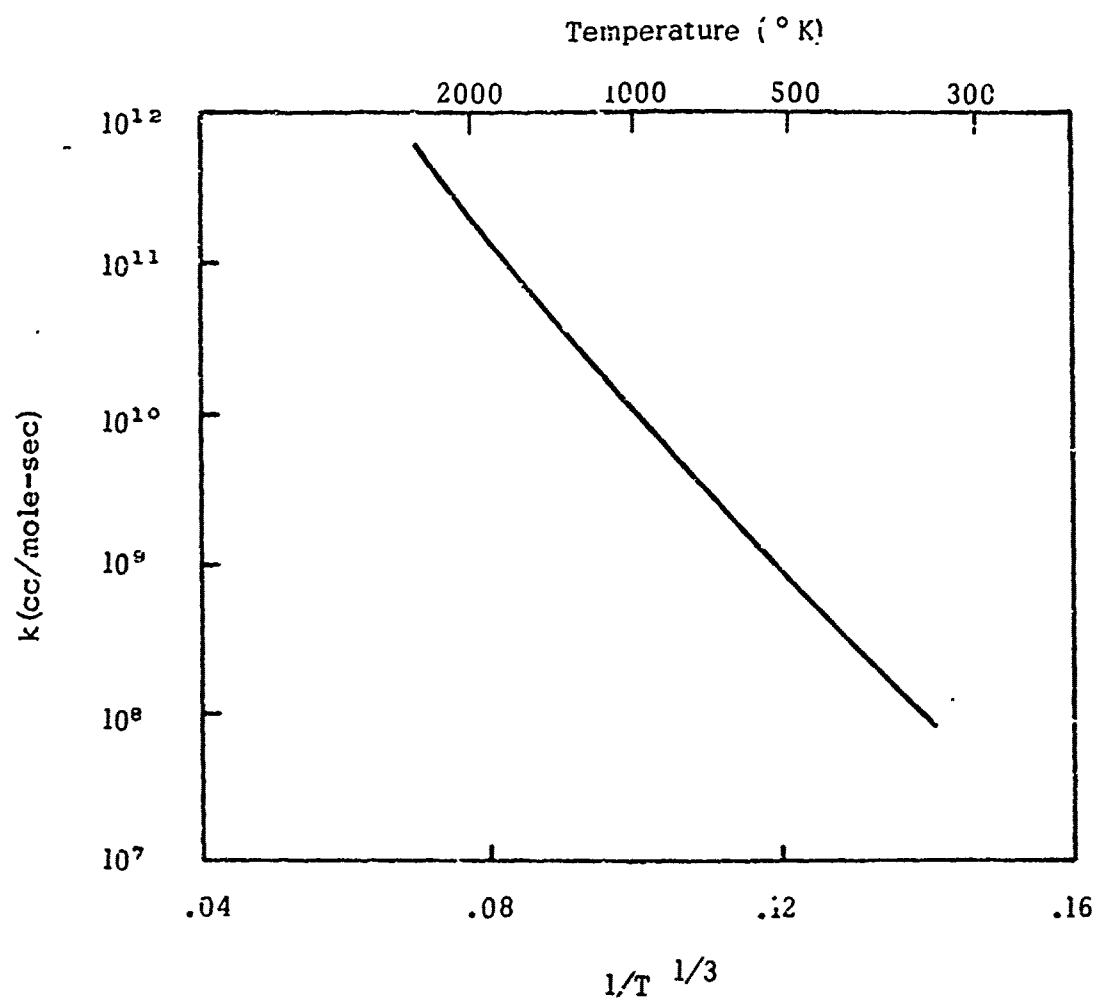


Figure 10 Review of experimental results for the deactivation of $H_2(l)$ by H_2



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