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VIBRATIONAL RELAXATION IN EXPANDING N_2 AND AIR

By Daniel I. Sebacher and Robert W. Guy

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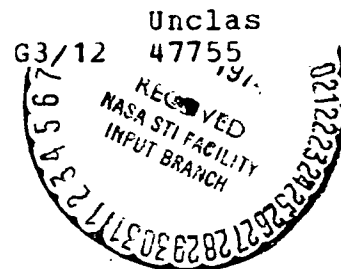
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SUMMARY

New N_2 vibrational temperature data, obtained in expanding N_2 and air using the electron beam technique, are analyzed permitting the vibrational relaxation times to be determined as a function of temperature. In addition, the effects on N_2 vibrational relaxation times of direct vibrational energy transfer between N_2 and H_2O, between N_2 and O_2, and between N_2 and free electrons introduced from arc contaminants are analyzed. The vibrational relaxation times determined from the present measurements agree with those measured in the expanding flows of shock tunnels and impact tubes. These expanding data also agree with relaxation times observed in acoustical resonant cavities where alternating compressions and expansions take place. The relaxation times in expanding flows (vib-tran exchange process) are found to be approximately 50 times faster than those measured in the compressing flow of shock tubes (tran-vib exchange process). This evidence strongly supports the concept that one relaxation time distribution cannot be applied to both exchange processes.

INTRODUCTION

The excitation and de-excitation of the vibrational energy of N_2 has been the subject of many theoretical and experimental investigations (ref. 1). The basic theory of Landau and Teller (ref. 2), further developed by Schwartz, Slawsky and Herzfeld (SSH) (ref. 3) and others, coincided with the development of various experimental diagnostic techniques. These techniques include: impact tube measurements (ref. 4), ultrasonic absorption (refs. 5 and 6), interferometry, schlieren and spectroscopy (refs. 7 to 13), and the analysis of light emitted from an electron beam (refs. 14 and 15). The measurements cover a wide range of gas temperatures with the original high temperature range being studied behind shock waves (ref. 7) and the original low-temperature range being studied in acoustical resonant cavities (ref. 6) and in impact tubes (ref. 4). Efforts were made to correlate these data, but as additional shock tube measurements became available (ref. 11), the correlation of the low-temperature data became poor and the low-temperature techniques were generally assumed to be in error because of effects of extraneous H_2O concentrations.

Many of the vibrational nonequilibrium flows of interest involve expansion environments where de-excitation of the vibrational state occurs. The prevailing assumption has generally been that the forward excitation relaxation times obtained in the compressing environments of shock waves could be applied

to the reverse de-excitation times of expanding flows. However, in recent years experimental measurements of vibrational temperature obtained in expanding flows using spectroscopic line reversal (refs. 13 and 16) and the electron beam technique (ref. 15) have consistently shown the forward excitation times obtained in compressing flows to be between one and two orders of magnitude too slow for vibrational de-excitation in expanding flows. Despite the fact that the faster times measured in expanding flows have come from a variety of facilities and several independent measuring techniques, the results do not appear to have gained general acceptance.

Another discrepancy in N_2 vibrational relaxation time data lies in whether a difference exists in relaxation times in pure N_2 and in N_2 in air. A previous attempt (ref. 17) to correlate the available data obtained in expanding flows failed to show any difference. However, such a difference was observed in the compressing flow data from shock tubes (ref. 12).

The objectives of this study are to assess the new data in relation to other relevant N_2 vibrational relaxation data found in the literature, to clarify the discrepancies listed above, and to correct these data as influenced by H_2O content.

SYMBOLS

a	mole fraction of gas A (N_2 in this paper)
c	mass fraction
c_p	heat capacity
E	vibrational energy per unit volume
H	enthalpy
h	Planck's constant
k	Boltzmann's constant
P	transition probability
p	pressure
R	gas constant
T	temperature
t	time
v	vibrational levels

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Z	collision number at one atm and temperature T
α	vib-vib coupling term derived in reference 22
θ	characteristic temperature ($h\upsilon/k$)
υ	characteristic frequency
σ	vibrational energy per unit mass
τ	vibrational relaxation time

Subscripts:

A	gas A (N_2 in this paper)
B	gas B
eff	effective
t	total
v	vibrational

Superscripts:

e	indicates in equilibrium with the translational temperature
v	indicates vib-vib energy transfer

APPARATUS AND TESTS

Tunnel and Test Conditions

This investigation was conducted in a wind tunnel where N_2 or air is heated as it flows through a magnetically rotated electric arc into a stagnation chamber. The hot gas then flows through a 5.5 mm diameter sonic throat and expands through a 5° half-angle conical nozzle to a 0.305-meter diameter, closed-jet test section.

Tests were conducted for stagnation chamber temperatures ranging from 1480 to 4720 K and stagnation chamber pressures ranging from 4.05×10^5 to 8.11×10^5 N/m^2. Test section Mach number ranged from 11.2 to 12.6. Flow conditions did not vary during a given test.

Test section flow properties were obtained by using pitot pressures measured on each test to enter nonequilibrium flow computer programs. This procedure had previously been verified in a tunnel calibration (ref. 18).

Total Enthalpy Determination

Total enthalpy inaccuracy could account for the previous inability to differentiate between the N_2 vibrational relaxation times in pure N_2 and in air (ref. 17). Total enthalpy for those tests was determined using the sonic throat technique as described in reference 18. However, this technique has been found to be in error at the higher enthalpies produced in this particular wind tunnel. The error is caused by gas swirl (induced by the magnetically rotated electric arc) affecting the stagnation chamber pressure which is required in the sonic throat technique.

Since the sonic throat technique was not dependable, the total enthalpy of the tunnel was measured in both air and N_2 using a tube calorimeter which swallowed the total gas flow issuing from the tunnel throat (refs. 18 and 19). Using these calorimeter results, the total enthalpy can be found within $\pm$ 10 percent over the temperature range of the present experiment.

Electron Beam Techniques

The electron beam technique for measuring N_2 vibrational temperatures has been discussed in the literature (refs. 14 and 15), so only a brief description will be given here. In this technique, an electron gun produces a narrow column of electrons which pass normal to the flow and through the test section. These fast electrons excite a small number of the flowing N_2 molecules and de-exciting molecules emit light which is dominated by the first negative system of N_2^+. The relative intensity ratio of the total light emission from the (0,1) and (1,2) bands of N_2^+ is used to determine the N_2 vibrational temperatures from an expression derived using the Franck-Condon Principle (refs. 15, 20, and 21). This principle states that the electron jump in the molecule is so fast relative to the intermolecular motion that the internal motion of the molecule does not have time to adjust. Consequently, the thermal distribution of the N_2 ground state can be determined from the electron beam excited N_2^+.

In the present experiment, a 15 kV electron beam was used and the light emission was observed through quartz windows using a 1/2-meter spectrograph. The entrance and exit slits of the spectrograph were adjusted so that the (0,1) and (1,2) bands of N_2^+ were just resolved in the first order. This was accomplished by using a photoelectric readout fed to a microammeter whose output was displayed on a strip recorder.

THEORY OF VIBRATIONAL RELAXING GASES

The following analysis treats the nozzle flow as a quasi one-dimensional expansion process. The degrees of freedom of the gases are grouped into active and inert with local thermodynamic equilibrium assumed within the two groups but not between them. With only the relaxation of the vibrational

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degrees of freedom assumed, the enthalpy can be written as

$$H = c'_p T + \sigma \tag{1}$$

where c'_p is the heat capacity for only the translational and rotational energy modes. The vibrational energy per unit mass σ can be calculated for N_2 by assuming the harmonic oscillator model

$$\sigma_{N_2} = \frac{R_{N_2} \theta_{N_2}}{\exp \dfrac{\theta_{N_2}}{T_v} - 1} \tag{2}$$

and for a mixture of gases A and B by

$$\sigma = C_A \frac{R_A \theta_A}{\exp \dfrac{\theta_A}{T_v} - 1} + C_B \frac{R_B \theta_B}{\exp \dfrac{\theta_B}{T_v} - 1} \tag{3}$$

Calculation of flow parameters in a nozzle for relaxing conditions requires a rate expression of the Landau-Teller type which for N_2 is

$$\frac{d\sigma_{N_2}}{dt} = \frac{\sigma_{N_2}^e - \sigma_{N_2}}{\tau_{N_2}} \tag{4}$$

where σ_{N_2} is the vibrational energy at the local vibrational temperature and $\sigma_{N_2}^e$ is the vibrational energy in equilibrium with the translational temperature.

The energy relaxation equation for an A molecule in a binary gas mixture of A and B molecules, including the vib-vib exchange, is given by Schwartz, Slawsky and Herzfeld (SSH) (ref. 3) as

$$a \frac{dE_A}{dt} = \left[\frac{a}{\tau_{AA}} + \frac{1-a}{\tau_{AB}} \right] (E_A^e - E_A) + \frac{a(1-a)}{\tau_{AB}^v} \left[E_B \frac{E_A^e - E_A}{E_B^e} \left(\frac{1 - \exp(-\frac{\theta_A}{T})}{1 - \exp(-\frac{\theta_B}{T})} \right) - E_A \frac{E_B^e - E_B}{E_B^e} \right] \tag{5}$$

The vibrational relaxation times τ_{AA} and τ_{AB} for the vib-tran processes are

$$\tau_{AA} = \left[P_{AA} Z_{AA} \left(1 - \exp\left(-\frac{\theta_A}{T} \right) \right) \right]^{-1} \tag{6}$$

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$$\tau_{AB} = \left[P_{AB} Z_{AB} \left(1 - \exp\left(-\frac{\theta_B}{T} \right) \right) \right]^{-1} \qquad (7)$$

where P_{AA} is the probability that during a collision between two A molecules one makes the vibrational transition $v = 1$ to $v = 0$ with that energy ending up in the relative translational energy of the collision pair. P_{AB} is the similar probability for the A and B molecules. Z is the number of collisions per second for the molecules designated at one atmosphere and at temperature T computed by the usual classical methods.

The relaxation time for the vib-vib process τ_{AB}^{v} is

$$\tau_{AB}^{v} = \left[P_{AB}^{v} Z_{AB} \right]^{-1} \qquad (8)$$

P_{AB}^{v} designates the probability that during a collision, molecule A makes a transition $v = 1$ to $v = 0$, while B goes from $v = 0$ to $v = 1$ with the excess energy taken up in translation.

The rate expression for air where $A = N_2$ and $B = O_2$ can be simplified since it is known that $\tau_{AB}^{v} << \tau_{AA} + \tau_{AB}$ and $\tau_{BB} + \tau_{BA} << \tau_{AA} + \tau_{AB}$. It has been shown experimentally (refs. 22 and 23) and analytically (ref. 24) that under these conditions each component in the mixture has the same effective vibrational relaxation time τ_{eff} greater than τ_{O_2} and less than τ_{N_2} since the N_2 acts as an additional reservoir of vibrational energy during the establishment of equilibrium of O_2 and, consequently, of the entire mixture. The rate expression for the relaxing N_2 in a binary mixture under these assumptions can therefore be given by

$$\frac{d\sigma_{N_2}}{dt} = \frac{\sigma_{N_2}^{e} - \sigma_{N_2}}{\tau_{eff}} \qquad (9)$$

This rate equation together with the usual gas dynamic equations and thermo-dynamic relations completely describe the vibrational relaxation of a gas in a nozzle expansion without transport or wall effects. These equations were solved numerically to allow evaluation of the test data. Details of this technique can be found in reference 25.

The τ_{eff} from the experimental data can be used to determine the vib-vib relaxation time through an expression derived by Taylor, et al. (ref. 22) relating τ_{AB}^{v} and τ_{eff}

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$$\tau_{AB}{}^{v} = (1 - a) \left[\frac{1 - \exp\left(-\frac{\theta_A}{T}\right)}{1 - \exp\left(-\frac{\theta_B}{T}\right)} - (1 - \alpha) \right] \tau_{eff} \tag{10}$$

where α is a coupling term defined in reference 22 which varies from 0 (strong coupling) to 1 (weak coupling). To correct the data for small concentrations of water vapor (gas B) in N_2 (gas A), where $(1 - a) \ll 1$, the effective transition probability for collision is written as

$$P_{eff} = a\, P_{AA} + (1 - a)\, P_{AB} + (1 - a)\, P_{AB}{}^{v} \tag{11}$$

Using equations (6), (7), and (8) it can be shown that equation (11) is identical to equation (10) for the resonant case $\theta_A = \theta_B$ and $\alpha = 1$ when the H_2O concentration is great enough so that only the last term on the right is significant. $P_{AB}{}^{v}$ generally is two orders of magnitude greater than P_{AA} or P_{AB}.

RESULTS AND DISCUSSION

N_2 Vibrational Relaxation in N_2 and Air

N_2 vibrational temperatures measured in expanding N_2 and air using the electron beam are shown as a function of total temperature in figure 1. The predicted variations of the N_2 vibrational temperatures shown were computed using the nonequilibrium flow programs (refs. 18 and 25) in which the vibrational rate expression could be varied. The measured N_2 vibrational temperatures in pure expanded N_2 are consistently lower than those predicted by the shock tube relaxation times above a stagnation temperature of 2000 K. Below 2000 K the vibrational temperature becomes increasingly insensitive to variations in relaxation time. To evaluate the data the relaxation time expression was assumed to have the well known form

$$\tau p = D \exp \left(FT^{-1/3}\right) \tag{12}$$

where the constants D and F are evaluated using the nonequilibrium program. The τp expression that best fits the measured N_2 vibrational temperatures shown in figure 1 is

$$\tau p_{N_2} = 3.4 \times 10^{-12} \exp \left(195\, T^{-1/3}\right) \tag{13}$$

where τ is in seconds, p is in atmospheres and T is in degrees Kelvin.

The N_2 vibrational temperatures measured in expanded air, also shown in figure 1, remain lower than the expanded N_2 measurements and appreciably lower than the predicted vibrational temperature using the relaxation times measured for air in a shock tube (ref. 12). The expression for τp that best fits the air data is

$$\tau p_{air} = 1.2 \times 10^{-10} \exp (130\ T^{-1/3}) \tag{14}$$

with the same units as listed above.

Dissociation and recombination nonequilibrium effects in the air flow were accounted for by use of the CAL chemical nonequilibrium program (ref. 26), and vibrational nonequilibrium was accounted for by adding the sudden freeze technique to this program (refs. 18 and 27). The relaxation times determined in expanding N_2 and air are both on the order of 50 times faster than their respective values measured in the compressing flow of shock tubes.

The expression τp (eq. (13)) for vibrational relaxation in expanding N_2 is plotted in figure 2 as a function of $T^{-1/3}$ along with the shock tube data (refs. 7 to 12), acoustical data (refs. 5 and 28), impact tube data (ref. 4), the distribution determined in a shock tunnel (ref. 29) and the SSH prediction (refs. 3 and 30). The impact tube data have been corrected for H_2O effects on τp as will be explained.

These results indicate two trends of agreement, one for the various shock tube data (compressing flow) and another in which the data from all the other techniques (expanding flows) are in accord. The present relaxation time data correlate with those measured in shock tunnels and impact tubes where the expanding gases provide the vib-tran rate. These measurements are also shown to agree with relaxation times observed in acoustical resonant cavities where alternating compressions and expansions take place. Measurements made in unsteady expansion waves in shock tubes (ref. 16) are also in general agreement with the expansion data. The relaxation times from the correlation of the expanding flow data (vib-tran) are found to be approximately 50 times faster than those obtained from the shock tube data (tran-vib). Also, the expanding flow relaxation times are about 6 times faster than the times predicted by the SSH theory.

A number of reasons have been suggested for the different relaxation observed in vibrational excitation and de-excitation. Two of these arguments which have been treated analytically are the effects of anharmonic oscillation and the dependence of de-excitation on interaction potentials. Bray (ref. 31) and Rich and Rehm (ref. 32) have concluded that the anharmonicity would not significantly affect the rate of vibrational excitation, or the relaxation rate near equilibrium. However, sufficiently far from equilibrium, as in an expanding flow, they determined that the vibrational de-excitation rate greatly increases as a result of an upper-level population reversal, fed by rapid vib-vib exchanges.

Shin (ref. 33) analyzed the inclusion of an attractive as well as a repulsive portion of the interaction potential for both the Morse and Lennard-Jones potentials, and his analysis results in a number of correction terms. He shows (at 600 K) that by assuming a Morse potential, the de-excitation probability for the $N_2 - N_2$ system may increase by a factor of 5.8 when the attractive part is included. This increase in the rate is of the same order measured in the expansion from that predicted by the SSH theory.

<div align="center">H_2O Effects on τ</div>

Corrections made on the impact tube data (ref. 4) for the effects of H_2O made use of equation (11) and the τ to Z relations given in equations (6), (7), and (8). To do this $P^V_{N_2H_2O}$ was taken from the line drawn through the data shown in figure 3. This line is drawn to favor the data of reference 34 because these data agree with the SSH theory for vib-vib transfer for N_2 and H_2O. The vib-vib transfer probability is about two orders of magnitude greater than the probability of vib-tran transfer. With the small concentration of H_2O for the impact tube data, $(1 - a) = 5 \times 10^{-4}$, the second term on the right of equation (11) is insignificant and $P_{N_2N_2}$ can be evaluated by adjustment until a selected value gives P_{eff} computed equal to the P_{eff} given by Huber and Kantrowitz (ref. 4). This correction is possible only if the $P_{N_2N_2}$ remains in the range of the expanded data or higher. If it were an order of magnitude less, the first term on the right of equation (11) would also be insignificant, and P_{eff} would only depend on $P^V_{N_2H_2O}$ and the H_2O concentration. Since Huber and Kantrowitz measured the N_2 relaxation time in the expansion through a nozzle, the assumption made here is believed valid. The corrected values of reference 4 are:

T(K)	Measured τp atm-sec.	Corrected τp atm-sec.
556	5.9×10^{-3}	1.7×10^{-2}
680	2.9×10^{-3}	8.1×10^{-3}
686	2.7×10^{-3}	7.0×10^{-3}
694	3.4×10^{-3}	1.7×10^{-2}
761	2.6×10^{-3}	1.5×10^{-2}

In order to determine any effects of small concentrations of H_2O on the present measurements, the H_2O mole fraction was varied from 10^{-5} to 10^{-4} in pure N_2 with the amount of H_2O present being determined using a dew point indicator. No measurable effects were observed within the scatter of the data as would be expected from a simple calculation using equation (11). At $T^{-1/3} = 0.08$ (t = 1950 K), $P^V_{N_2H_2O} = 2.55 \times 10^{-3}$ from figure 3, and $Z_{N_2N_2} =$

2.1 x 10^9 coll/sec. Taking $\tau_{N_2N_2}$ = 2 x 10^{-5} sec from equation (13), or figure 2, and letting (1 - a) = 10^{-4}, then

$$P_{eff} = P_{N_2N_2} + (1 - a) P^V_{N_2H_2O} = 2.38 \times 10^{-5} + 2.55 \times 10^{-7}$$

thus showing that P_{eff} or τ_{eff} is not significantly greater than $P_{N_2N_2}$ or $\tau_{N_2N_2}$. When one analyzes the shock tube data for the same amount of H_2O then

$$P_{eff} = 7.3 \times 10^{-7} + 2.55 \times 10^{-7}$$

While this H_2O effect appears to be about half the value of $P_{N_2N_2}$ or $\tau_{N_2N_2}$, it cannot explain the difference between the compressing flow data from shock tubes and the expanding flow data. The adjustment of the shock tube data due to this concentration of H_2O is within the scatter of these data as seen in figure 2. The dried air used in the present study was monitored by a dew-point indicator and had an H_2O mole fraction of less than 2 x 10^{-4}. The H_2O concentrations of 0.005 percent given for the acoustical data of reference 6 were so small that any correction would again be insignificant. No concentrations of H_2O were given in references 5 and 30.

Arc Impurity Effects on τ

Hurle (ref. 35) has analyzed the effectiveness of energy transfer between free electrons from contaminants and N_2 molecular vibration. Even though the concentration of arc contaminants may be small, the free electrons produced from them in the electric arc have a probability of energy exchange with the N_2 vibrational mode which is at least two orders of magnitude greater than the probability for the N_2 - N_2 vib-tran exchange. The free electron concentration has been measured in the test stream of the arc tunnel using a microwave interferometer and a Langmuir probe (ref. 36). The value found in N_2 is approximately constant over the temperature range of this experiment at a value of 10^{10} electrons per cm^3. This would be equivalent to an electron mole fraction ratio of 5 x 10^{-6} which would be far too small to effectively reduce the relaxation time of the N_2 according to Hurle (ref. 35).

N_2 Vibrational Relaxation in Air

The expression for τp (eq. (14)) which best fits the present data for vibrational relaxation of N_2 in expanding air is shown plotted in figure 4 as a function of $T^{-1/3}$ along with the expression determined from the present data for expanding pure N_2. Also, plotted in this figure are expressions

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fitted to the shock tube data for N_2 and air. A similarity exists between these curves for the two gases in that the difference measured between relaxation times in compressing and expanding air is about the same order of magnitude as the difference measured between relaxation times in compressing and expanding N_2. Therefore, the expanded air relaxation times are approximately 50 times faster than those measured in shock tubes as was the case in N_2. The vib-vib probability of the $N_2 - O_2$ exchange was computed from the expanding air data using equations (8) and (10) and assuming that the coupling parameter α is equal to 0.75 (ref. 22). These probabilities determined from the experimental expansion data are compared in figure 5 to the SSH theory and some experimental data representative of that found in shock tubes (ref. 23). Similar to the vib-tran exchange, the measured vib-vib exchange probability is greater in an expanding gas and less in a compressing gas (shock tube) than the theoretical predictions.

CONCLUDING REMARKS

New N_2 vibrational temperature data, obtained in expanding N_2 and N_2 in air using the electron beam technique, are analyzed permitting the vibrational relaxation times to be determined as a function of temperature. In addition, the effects on N_2 vibrational relaxation times of direct vibrational energy transfer between N_2 and H_2O, between N_2 and O_2, and between N_2 and free electrons introduced from arc contaminants are analyzed.

The vibrational relaxation times determined from the present measurements agree with those measured in shock tunnels and impact tubes. These expanding data also agree with relaxation times observed in acoustical resonant cavities where alternating compressions and expansions take place. The relaxation times in expanding flows (vib-tran exchange process) are found to be approximately 50 times faster than those measured in the compressing flow of shock tubes (tran-vib exchange process). This evidence strongly supports the concept that one relaxation time distribution cannot be applied to both exchange processes.

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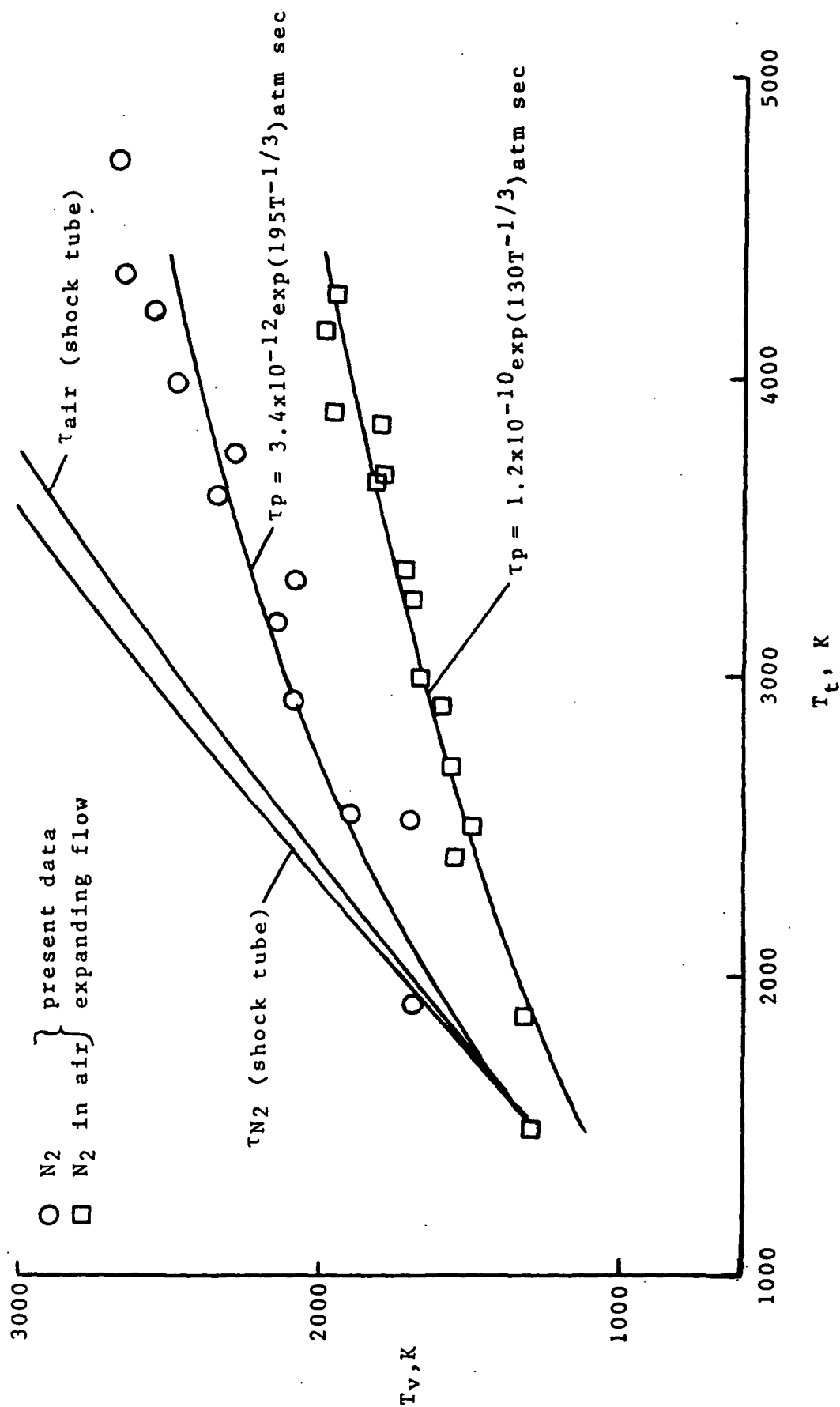
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Figure 1. — Measured and predicted N_2 vibrational temperature as a function of total temperature for pure N_2 and N_2 in air.
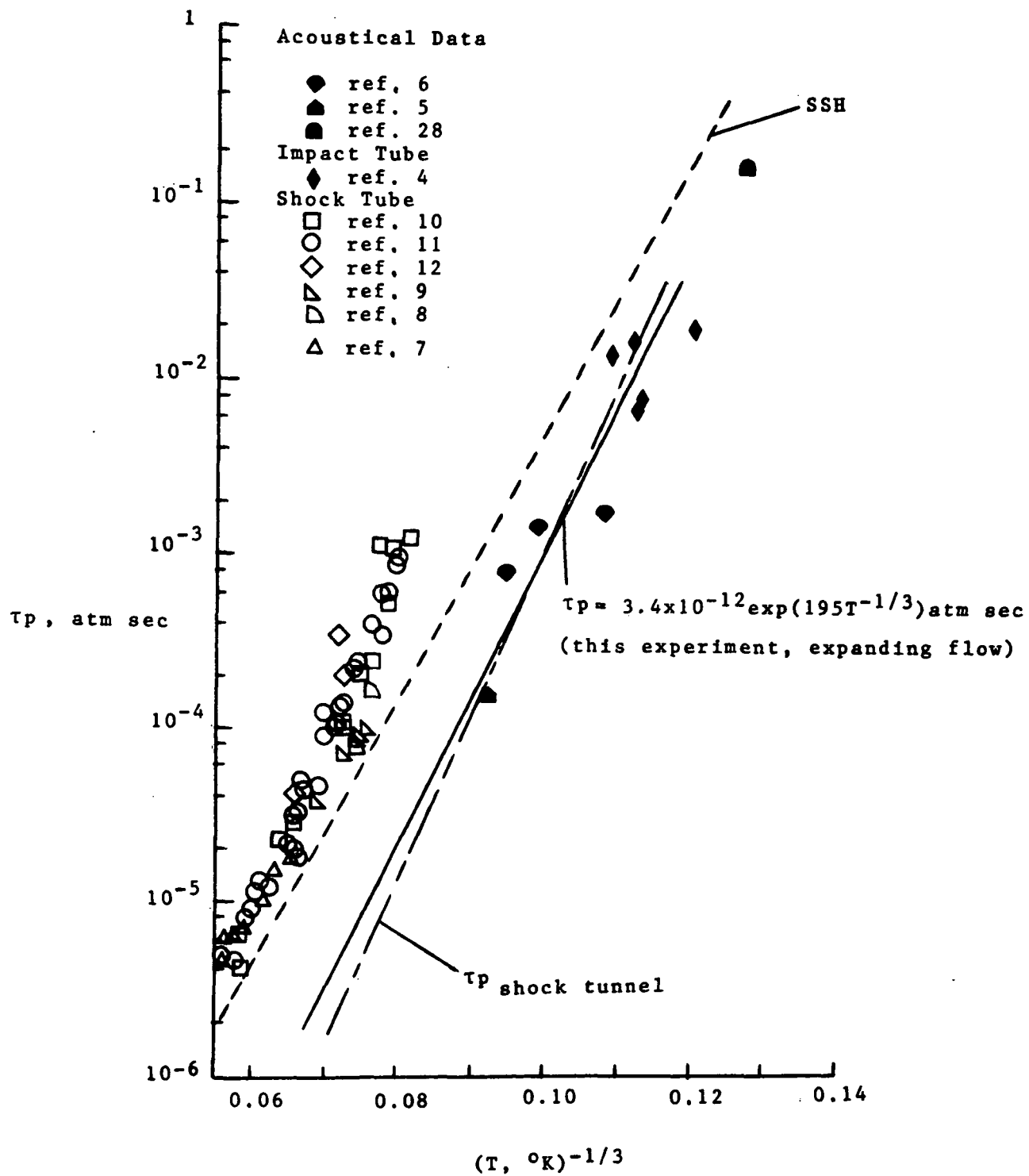
15

Figure 2. – Vibrational relaxation times for N_2 as a function of temperature.
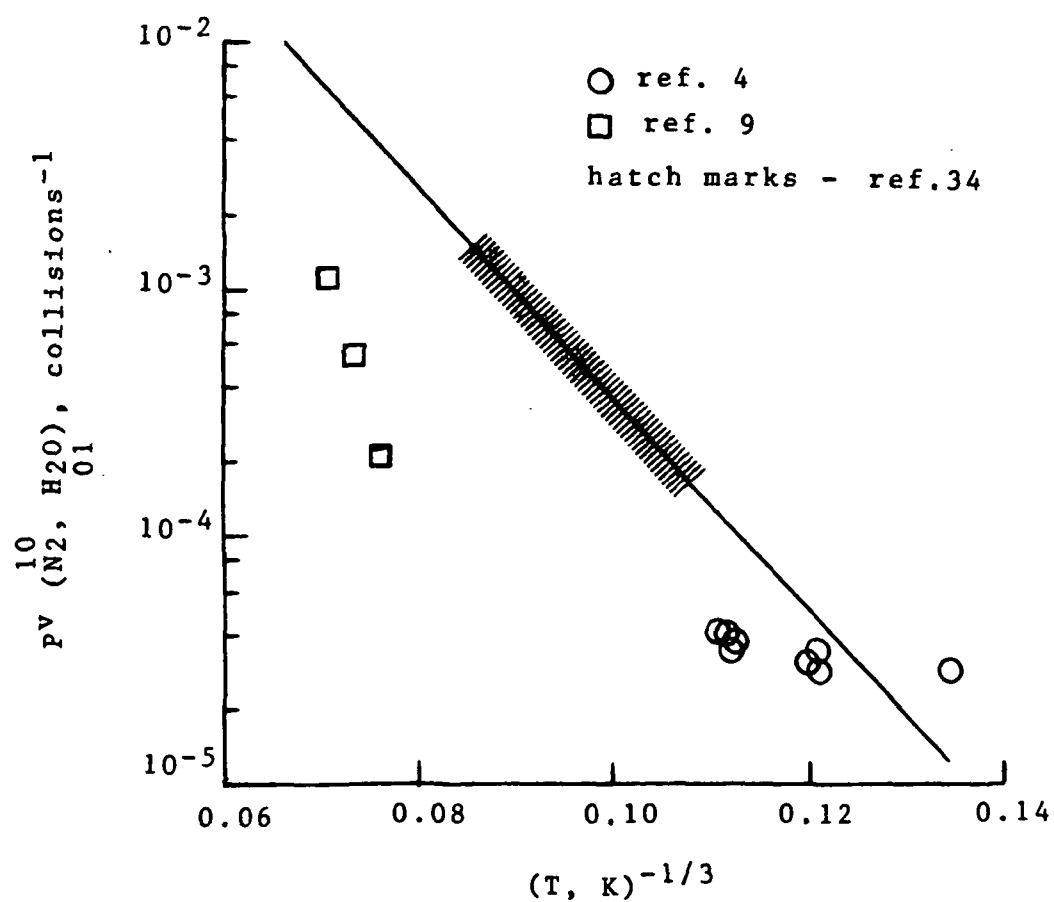
16

Figure 3.- Experimentally derived probabilities for vib-vib transfer from N_2 to H_2O as a function of temperature
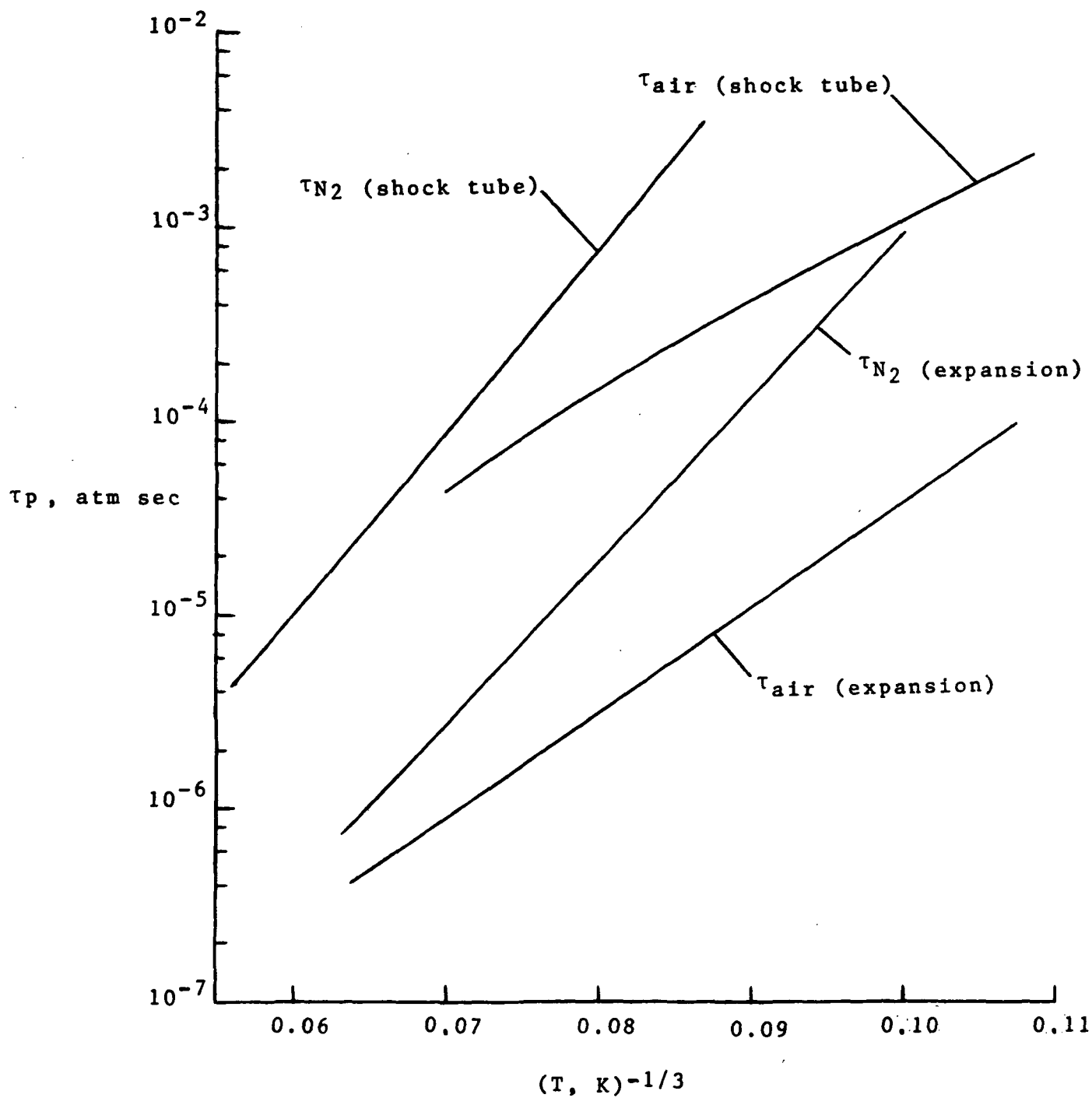
Figure 4. - Vibrational relaxation times for pure N_2 and
N_2 in air as a function of temperature derived
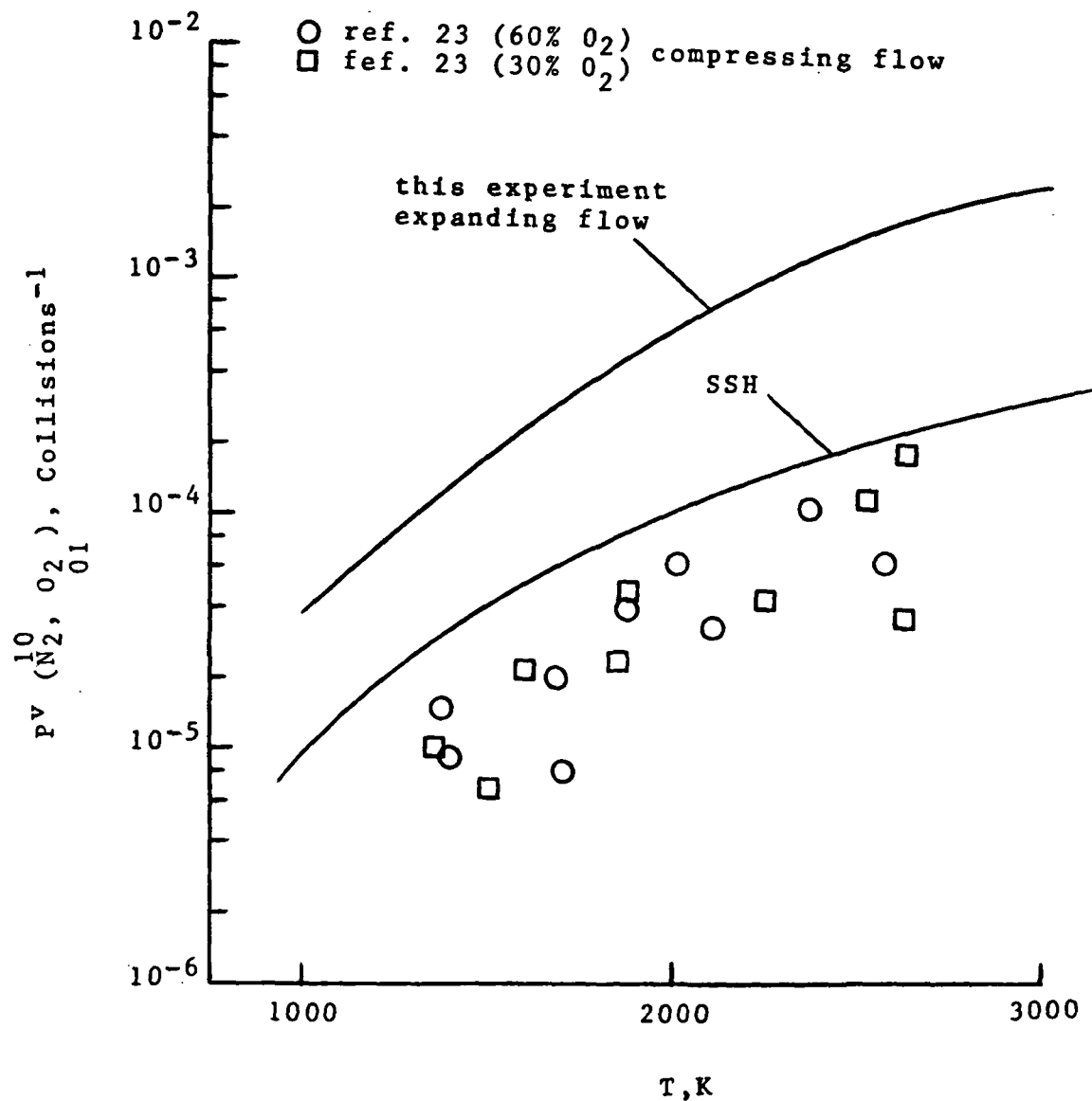from this experiment and from shock tube experiments.

Figure 5. - Probalities for vib-vib transfer from N_2 to O_2 as a function of temperature.