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# THE UNIVERSITY OF OKLAHOMA GRADUATE COLLEGE

# VIBRATIONAL RELAXATION OF CARBON MONOXIDE IN NON-EQUILIBRIUM NOZZLE FLOW

## A DISSERTATION

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## SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

#### degree of

DOCTOR OF PHILOSOPHY

### ΒY

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Norman, Oklahoma

#### 1968

# VIBRATIONAL RELAXATION OF CARBON MONOXIDE

IN NON-EQUILIBRIUM NOZZLE FLOW

. APPROVED BY asmusslu ni n.

DISSERTATION COMMITTEE

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#### VIBRATIONAL RELAXATION OF CO IN NON-EQUILIBRIUM NOZZLE FLOW

#### I. INTRODUCTION

Vibrational relaxation of gases is a subject important to the understanding of gas properties and behavior at high temperatures. The temperature at which vibrational energy becomes an important fraction of the total energy content of gas is approximately that temperature at which kT (where kis Boltzmann's constant and T is the gas temperature) is equal to the energy of the first excited vibrational quantum level of the gas. For diatomic molecules such as  $O_2$ ,  $N_2$ , or CO this temperature is about 2000<sup>°</sup>K to 3000<sup>°</sup>K. Such temperatures are commonly encountered behind shock waves in supersonic flight and in combustion processes such as in rocket motors and jet engines. There are many other situations in which vibrational non-equilibrium is important. In a chemical reaction new species can be formed in vibrational states not only out of equilibrium with the translational temperature but in a non-Boltzmann distribution among vibrational states. An electrical discharge in nitrogen will cause its vibrational energy to be excited out of equilibrium due to the transfer of energy from electrons to nitrogen vibration. Gas lasers radiating in the infrared operate by virtue of non-equilibrium vibrational excitation.

The term vibrational relaxation implies a non-equilibrium situation in which the vibrational energy is out of equilibrium with the translational energy but is "relaxing" toward equilibrium. A simple example of this can be found behind a shock wave. Gas flowing through a shock wave has its translational energy suddenly increased in the distance of a few mean-freepaths of the unshocked gas. Thus, with just a few collisions per molecule

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the gas has changed the state of its translational energy from that of an equilibrium gas with a Maxwell distribution of molecular velocities at temperature  $T_1$  to that of a gas at temperature  $T_2$ . The rotational energy of the gas requires a similar number of collisions to change its state from being in equilibrium with translation at temperature  $T_1$  to equilibrium at temperature T<sub>2</sub>. The vibrational energy however is slower to adjust simply because for each collision of one molecule with another, the probability of there being an exchange of energy between translation and vibration (or even rotation and vibration) is considerably smaller than probabilities for the other exchange processes. Thus immediately behind a shock wave the translational and rotational energy are characterized by the temperature  $T_2$ , while the vibrational energy is still characterized by the temperature  $T_1$ . The time that is required for the vibrational energy to come into equilibrium. with translation and rotation is termed the vibrational relaxation time or just the relaxation time. In the next section the relaxation time and temperatures for a gas not in equilibrium will be defined in a more precise manner.

It is important to recognize that in the relaxation region behind a shock wave the energy transfer is from translation and rotation to vibration. An example in which the energy transfer occurs in the opposite direction is a nozzle flow. In this situation the gas is initially in an equilibrium state in the <u>stagnation region</u>; from this state it expands down the nozzle. In this rapid expansion flow the gas temperature drops quickly as it does the vibrational temperature also tends to decrease due to transfer of vibrational energy to translation and rotation through collisions. If this transfer process cannot keep up with the rapid temperature drop, then the gas becomes out of equilibrium -- it has an excess of vibrational energy which it must transfer to translation before equilibrium can be reached.

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Relaxation times have been measured behind shock waves " and applied to a wide variety of flow situations. For the case of the simple diatomic molecule relaxing either by itself or in a mixture with an inert diluent the situation seemed well understood. The theory of vibrational relaxation<sup>2, 3, 4</sup> correctly gave the temperature and pressure dependence of the relaxation time; further it indicated no dependence of this time on the vibrational state of the gas so, for example, one could apply the relaxation time measured behind shock waves to all situations, including the relaxation in a nozzle flow. Recently, however, considerable experimental evidence has been put forth indicating that the vibrational relaxation of nitrogen and carbon monoxide is faster when the gas is being cooled (as in a nozzle expansion) than when the gas is heated (as in the relaxation following a shock wave). This discrepancy in the relaxation times has been expressed by the ratio  $\phi = \tau_s / \tau_e$  where  $\tau_s$  is the relaxation time measured ' behind a shock wave and  $au_{
m p}$  is the relaxation time deduced from an expansion flow experiment.

The first measurements of vibrational relaxation in an expansion flow were by Hurle, Russo and Hall<sup>5</sup>, at the Cornell Aeronautical Laboratory (CAL). They examined nitrogen by using a shock tunnel to generate a nozzle flow with stagnation temperatures and pressures of 2800° to 4600°K and 24 to 82 atm, respectively. They measured the vibrational temperature in the supersonic portion of the nozzle by means of a line reversal technique

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<sup>&</sup>lt;sup>\*</sup>Many measurements and, in fact, the earliest measurements of vibrational relaxation times have been by ultrasonic dispersion. 1, 2 However for the measurement of relaxation times at temperatures above 1000<sup>o</sup>K of the common diatomic species which we are concerned with here, this technique has been surpassed by the more direct measurements behind shock waves.

and deduced that the relaxation time for nitrogen in their experiments was 15 times faster than its value behind shock waves (i. e.  $\phi = 15$ ). Later their results were re-examined, compared to more reliable shock tube data, and this conclusion was modified to  $\phi = 70$ . In a similar experiment Hall and Russo<sup>6</sup> examined a mixture of 5% CO-95% argon at stagnation temperatures and pressures of  $3500^{\circ}$  to  $5500^{\circ}$ K and 45 atm, and deduced that  $\phi = 100$ for CO in this mixture. Recently, Russo<sup>7</sup> reported infrared band reversal measurements on 5% CO in argon and found  $\phi = 1000$ .

Holbeche and Woodley<sup>8</sup> at the Royal Aircraft Establishment used a shock expansion tube and the sodium line reversal technique to observe the relaxation of CO and of N<sub>2</sub>; they obtained  $\phi = 15$  for nitrogen and no discrepancy for CO (i.e.  $\phi = 1$ ). However, their stagnation temperature and pressure of 2600°K and 8 atm were lower than the conditions examined at CAL. Sebacher<sup>9</sup> at NASA Langley used an arc heated nozzle flow with an electron beam technique to measure the vibrational and rotational temperatures of nitrogen in the nozzle and thereby examine the relaxation of nitrogen (T<sub>stag</sub> = 3100° - 5800°K) and nitrogen in air (2950° - 3980°K). In both cases he measured  $\phi = 15$ . Petrie<sup>10</sup> at Ohio State also used the electron beam technique to examine the vibrational relaxation of N<sub>2</sub> in air. His stagnation conditions were sufficiently high that his air consisted of almost fully dissociated oxygen, partially dissociated nitrogen, and 1.6% NO. He obtained  $\phi = 150$ compared to that for pure N<sub>2</sub>.

Hall and Russo, <sup>6</sup> and Holbeche<sup>8, 11</sup> have also examined the vibrational relaxation of oxygen in expansion, and found  $\phi = 1$  and  $\phi = 0.1$  (<u>slower</u> relaxation in expansion) respectively. Hall and Russo discount these results, however, due to complications arising from energetically low electronic states of oxygen.

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The experimental determinations of  $\phi$  in N<sub>2</sub> cannot be compared directly with each other, since each investigator made an independent choice of  $\tau_s$  on which to base his conclusions. A valid comparison is shown in Fig. 1, in which the various results for N<sub>2</sub> have been interpreted in terms of relaxation times and plotted vs temperature along with the most reliable shock tube measurements for this gas. A similar comparison is shown in Fig. 2 for the measurements which have been performed in CO.

These results indicate, collectively, that the relaxation times of nitrogen and carbon monoxide in a nozzle flow are around two orders of magnitude smaller than their values behind shock waves. This large effect has not been accounted for theoretically. Thus, until the effect is understood the experiments which suggest it must be carefully scrutinized. One relevant experiment for obtaining further evidence on the reality of this effect would be to use a passive measurement technique which does not require "seeding" the gas (as do the line reversal methods) or exciting the gas by external means (as does the electron beam technique) and, further, to pay close attention to gas purity. Gas purity has long been an area of concern in the measurement of relaxation times, because trace amounts of certain impurities can greatly reduce the relaxation time of a gas.

The work described here was initiated in October 1966, with the intent of fulfilling these two purposes. The vibrational relaxation of carbon monoxide in a shock tunnel was to be studied by using the CO infrared emission as a way of measuring its vibrational energy. A shock tunnel was to be used to generate the high temperature nozzle flow because it is a well developed device with calculable flow conditions, and a relatively controllable impurity

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level. Carbon monoxide was chosen as a test gas because it is infrared active, it has a high dissociation energy, its behavior in expansion had been examined by another technique, and its vibrational relaxation time has been reliably measured behind shock waves over a wide temperature range.<sup>12, 13</sup> Infrared emission is a good technique for measuring vibrational energy and thereby vibrational relaxation because it is passive, easily interpretable, and it is a well developed<sup>14, 12</sup> method for this purpose.

The following sections will present a basic discussion of vibrational temperature, energy and relaxation time, of CO infrared emission, and of shock tunnel operation. The experimental hardware, measurement technique, gas purity, and data analysis will be discussed in detail. Experimental results will be given for nozzle flows of 100% CO and 5% CO + 95% Ar along with measurements of the vibrational relaxation of CO by hydrogen atoms. Sources of experimental error will be reviewed. Finally, the results of this work and others will be discussed in terms of experimental uncertainties and in the light of recent theoretical results for expansion flow experiments.

#### II. THEORY

#### A. Vibrational Energy, Temperature, and Relaxation

A diatomic molecule stores vibrational energy in quantized levels whose energy spacing is determined by the potential which binds the two atoms of the molecule together and by the atomic masses. If the "potential well" is <u>harmonic</u> (i.e. the force between the atoms varies as the square of the interatomic separation) then the energy spacing is constant and the energy of leve, v relative to the ground state is just

$$\mathbf{E}_{\mathbf{v}} = \mathbf{v} \mathbf{h} \mathbf{v} \tag{II-1}$$

where h is Planck's constant and v is the frequency of vibration which would be given by classical analysis of the vibrator. The ground state energy of 1/2 h v plays no role here as only energy <u>changes</u> will be important. The potential energy function for real molecules is not harmonic but anharmonic; nevertheless, one can approximate the lowest energy levels (say  $v \le 5$ ) quite well with a harmonic function. This is useful because for temperatures below that for which dissociation is appreciable, and thus for temperatures of interest in this work, very few molecules are excited into higher energy levels. The distribution of molecules among the vibrational energy states at temperature T is determined at equilibrium by statistical mechanics as

$$\overline{n}_{v} = n \frac{e^{-E_{v}/kT}}{\sum_{v \in v} e^{-E_{v}/kT}}$$
(II-2)

n = number density of molecules  $cm^{-3}$   $\overline{n}_{v}$  = number density of molecules in  $cm^{-3}$ vibrational level v for equilibrium

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It is the exponential dependence of  $n_v$  on  $E_v$  or the "Boltzmann factor" which precludes molecules from populating the higher vibrational levels.

The total vibrational energy of the gas minus the ground state energy is just

$$\overline{\sigma} = \frac{1}{\rho} \sum_{v=1}^{\infty} E_v \overline{n}_v . \qquad (II-3)$$

 $\overline{o}$  = vibrational energy per unit mass for a erg/gm gas in equilibrium  $\rho$  = mass density of the gas gm/cm<sup>3</sup>

If one combines the preceding three equations and performs the summations involved, an expression for vibrational energy is obtained:

$$\overline{\sigma} = \frac{R \theta}{e^{\theta/T} - 1} \quad . \tag{II-4}$$

 $R = \frac{n}{\rho} k \text{ (or the universal gas constant} erg/cm-^{O}K$ divided by the molecular weight)

 $\theta = \frac{h\nu}{k}$ , characteristic temperature for <sup>o</sup>K vibration ( $\theta = 3090^{\circ}$ K for CO)

Notice that  $\theta$  is equivalent to the temperature which was mentioned in the introduction as a measure of where vibrational energy becomes significant. Sometimes it is convenient in discussing a non-equilibrium flow to speak of a vibrational temperature as distinct from the translational temperature or gas temperature. When this is done it is assumed that the molecules are in a Boltzmann distribution among the vibrational energy levels. The distribution is then described by equation (II-2) with an appropriate temperature, termed the vibrational temperature, T<sub>w</sub>. If such a Boltzmann distribution exists, and the total energy in vibration ( $\sigma$ ) is known, then equation (II-4) also serves to define T<sub>v</sub>; inversion of this equation gives T<sub>v</sub> explicitly as

$$T_{v} = \frac{\theta}{\ln \left(\frac{R \theta}{\sigma} + 1\right)} \quad . \tag{II-5}$$

Finally, if the gas is out of equilibrium and a Boltzmann distribution of molecules among the vibrational energy levels does <u>not</u> exist, one can speak of the vibrational temperature of a particular vibrational energy level. Such a temperature is defined by relating the population of a vibrational level j to the ground state through a Boltzmann factor:

$$\frac{n_j}{n_0} = e^{-E_j/kT_j}$$
(II-6)

Thus, given the ratio of the number of molecules in vibrational level j to the number in the ground state, equation (II-6) defines a vibrational temperature for the  $j \frac{th}{t}$  level. These vibrational temperatures for individual levels are introduced strictly for the convenience they will provide in discussing certain non-equilibrium situations.

In the measurements behind shock waves and in the nozzle flows described in this work, the rotational energy is assumed to be in equilibrium with the translational energy, so that the rotational temperature  $(T_R)$  is equal to the gas temperature (T). When a Boltzmann distribution in vibration simultaneously exists, this situation will be referred to as <u>quasi-equilibrium</u>. The distribution of molecules among rotational energy states (characterized by rotational quantum number J) is then determined by statistical mechanics.

$$\overline{n}_{J} = n \frac{g_{J} e^{-E_{J}/kT}}{\sum_{g_{J}} e^{-E_{J}/kT}}$$
(II-7)

E<sub>J</sub> = rotational energy of a molecule in rotational state J erg/molecule

 $g_T$  = degeneracy of rotational state J

$$E_{J} = \frac{h^{2}}{8\pi^{2} I} J (J + I)$$
 (II-7a)

 $g_T = 2 J + 1$  (II-7b)

I = moment of inertia of a molecule gm-cm<sup>2</sup>

The definition of the vibrational relaxation time comes about in a natural way as one derives the expression for the time rate of change of vibrational energy. The derivation of this expression begins with the <u>master</u> equation for vibrational energy transfer.

$$\frac{dn_{v}}{dt} = -\frac{k}{v}v, v+1 n_{v} + k_{v+1}, v n_{v+1} - k_{v,v-1} n_{v} + k_{v-1}, v n_{v-1}$$
(II-8)

 $k_{i_x,j} =$  fraction of molecules in vibrational sec<sup>-1</sup> level i that makes the transition to state j per unit time due to exchange of energy with translation

This equation already contains two assumptions: (1) that transitions only occur between adjacent vibrational levels, i.e.  $k_{i,j} = 0$  for  $j \neq i \pm 1$ .

(This is the radiation selection rule given by quantum mechanics for harmonic oscillators,) and (2) that there is no exchange of vibrational energy of one molecule with vibrational energy of another molecule. The second assumption can be realized in the case of diatomic molecules dilute in an infinite "bath" of inert (no vibrational energy) gas. For the case of a pure diatomic gas this second assumption is not met; however, it has been shown by Shuler<sup>15</sup> that with regard to the derivation of the time rate of change of vibrational energy which is outlined below, if the molecules can be considered as harmonic oscillators then the vibration-vibration exchange (V-V exchange) does not relax the vibrational energy but merely transfers vibrational quanta up and down the vibrational ladder. It thus tends to maintain a Boltzmann distribution of the molecules among the vibrational levels. This is true basically because the energy levels are equally spaced so that a V-V exchange is resonant and does not involve any energy exchange with translation. Further, since it is resonant there is a high probability for V-V exchange in any collision of two molecules; this ensures a Boltzmann distribution of molecules in vibration during relaxation. Consideration of effects due to anharmonicity will be deferred to the end of this work when experimental results are discussed; until then, vibrational relaxation will be considered within the framework of the harmonic oscillator approximation.

There are four rate constants in the master equation each of which can be written in terms of the rate constant  $k_{10}$  by the introduction of two relations. The first comes from the principle of detail balancing which demands that at equilibrium there is a balance of energy flux between any two energy states; thus

$$k_{v,v-1}\overline{n}_{v} = k_{v-1,v}\overline{n}_{v-1}$$
(II-9)

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$$k_{v-1,v} = k_{v,v-1} \frac{\overline{n}_{v}}{\overline{n}_{v-1}} = k_{v,v-1} e^{-\theta/T}$$
 (JI-10)

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where the last equality comes from invoking the Boltzmann distribution at equilibrium as given by equation (II-2). The second relation comes from using the radiative transition probabilities for a harmonic oscillator,

$$k_{v,v-1} = v k_{10}$$
 (II-11)

With these relations (II-9, 10, 11) and equation (II-8), the rate equation for vibrational energy relaxation as it appears in (II-12) can be derived<sup>4</sup> as

$$\frac{d\sigma}{dt} = k_{10} (1 - e^{-\theta/T}) \left\{ \overline{\sigma} - \sigma \right\} .$$
 (II-12)

The relaxation time is now conveniently defined as

$$\tau = \left\{ k_{10} (1 - e^{-\theta/T}) \right\}^{-1}$$
(II-13)

so that

or

$$\frac{d\sigma}{dt} = \frac{\overline{\sigma} - \sigma}{\tau} \quad . \tag{II-14}$$

This is the Bethe-Teller<sup>4</sup> equation for vibrational relaxation; it has been used for many years to calculate vibrational relaxation in a wide range of flow situations.

Since

$$k_{10} = Z P_{10}$$
 (II-15)

where

 $P_{10}$  = probability for de-excitation from the

first excited level to the ground state

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for a relaxing molecule

$$\mathbf{Z} = \sqrt{\frac{8\pi \,\mathrm{kT}}{\mu}} \,\mathrm{d}^2 \,\mathrm{n} \tag{II-16}$$

sec<sup>-1</sup>

and

- µ = reduced mass of relaxing molecule and gm
   its collision partner
- d = average collision diameter for the cm
  relaxing molecule and its collision partner
- n = number density of collision partners  $cm^{-3}$

the relaxation time and the probability for energy exchange in a collision are related in a simple way.

Calculation of the temperature dependence of  $\tau$  or  $P_{10}$  requires an analysis of the mechanics of the collision of a molecule with another particle. This analysis was first performed by Landau and Teller<sup>3</sup> who were able to show the major temperature dependence is represented by

$$k_{10} \sim e^{-T^{-1/3}}$$
 (II-17)

while the pressure dependence is determined by binary scaling since the relaxation is due to two-body collisions. Consequently,

$$\tau = \frac{1}{p} e^{T^{-1/3}}$$
 (II-18)

A plot of  $\ell n p\tau$  vs  $T^{-1/3}$  gives a straight line; thus data are usually presented on such a "Landau-Teller plot" (as for example Figs. 1 and 2).

Since vibrational relaxation involves a transfer of energy to or from translation, the gas temperature and other thermodynamic properties will

change during relaxation. One could in principle measure the time variation of any thermodynamic property and relate this through the conservation equations of gas dynamics with the vibrational energy in the energy equation, and deduce the relaxation time. For instance the use of an interferometer<sup>16, 12, 17</sup> to measure the change in gas density during the relaxation behind a shock wave is guite common. The most direct measurement, however, is to measure the vibrational energy or vibrational temperature itself. Four techniques which do this are: (1) the method of infrared emission<sup>14, 18</sup> which is applicable to heteronuclear molecules and measures directly the emission resulting from radiative transitions among the vibrational energy levels, (2) the line reversal technique<sup>5,19-22</sup> which measures emission from an electronic transition of a "seed" (trace amount of Na or Cr for example) whose electronic excitation is closely coupled to some vibrational level of the gas being examined, (3) the band reversal technique<sup>7</sup> which is similar to the line reversal method except no seed is required and the reversal temperature of the infrared band, or a portion of it, of a heteronuclear gas is measured, and (4) the electron beam method  $^{9,10}$ in which the gas is excited to an electronic state by means of an electron beam, in such a fashion that the vibrational and rotational distributions are undisturbed - spectroscopic analysis of the radiative de-excitation, which follows, reveals the vibrational and rotational temperatures of the gas. In this work, the method of infrared emission has been used to measure the vibrational relaxation of CO both behind shock waves and in nozzle flows; consequently the basic aspects of that method will be presented in the next section.

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#### B. Radiation and Measurement of Relaxation Times

Infrared emission of CO results from the spontaneous radiative decay of vibrational energy

$$CO (v = v_i) \rightarrow CO (v = v_j) + h\nu'$$
 (II-19)

Here  $h\nu'$  is the difference in energy of vibrational levels  $v_i$  and  $v_j$ . Transitions which involve the emission of a single quantum of vibrational energy  $(v_i - v_i = 1)$  make up the <u>fundamental band</u> around 4.6 $\mu$  wavelength, while those transitions which involve two quanta compose the first overtone band around 2.3 $\mu$ . The intensity of radiation resulting from these bands is related to the degree to which vibrational levels are populated and hence to the vibrational energy. If the gas has a Boltzmann distribution, then the population of vibrational levels decreases exponentially with increasing quantum number, and largest contribution to a band will be provided by the lowest vibrational level which can contribute to that band. Thus, in the first overtone band the  $v = 2 \rightarrow 0$  transitions are the largest contributors with smaller amounts of radiation coming from  $v = 3 \rightarrow 1$ ,  $4 \rightarrow 2$ , etc.; the fundamental band is dominated by the  $v = 1 \rightarrow 0$  transitions. This is one reason the overtone bands  $(\Delta v = 2, 3, etc.)$  are successively weaker. A more important reason is that the transition probabilities for multiple quantum emission are considerably smaller than those for single quantum decay; this results from the quantum mechanical selection rules which would forbid these multiple quantum transitions were it not for higher order effects due to anharmonicity and vibration-rotation interaction. Selection rules also specify for CO that each vibration transition be accompanied by a change in rotational quantum number of  $\Delta J = \pm 1$ .

The infrared <u>vibration-rotation</u> bands of CO are composed of many lines which are separated in wavelength for two reasons. The first is due to the non-uniform vibrational energy level spacing which results from the anharmonicity of the molecular potential. Because of this, radiation resulting from  $v = 1 \rightarrow 0$  transitions is not at exactly the same frequency as that coming from  $v = 2 \rightarrow 1$  transitions, etc. The second reason is due to non-uniform rotational energy level spacing (see equation (II-7a) and the coupling of a rotational transition with each vibrational transition; this spreading generates the P and R branches of a band. There are two points to be made here about the effect of this band structure. The first is the effect of the rotational temperature on band shape and band strength, and the second is the effect of band structure on the opacity of the band and the determination of the opacity of a band.

The effect of rotational temperature on band shape and band strength is important in the interpretation of radiation measurements because the detection system is calibrated from an equilibrium source of radiation such as a black body or hot equilibrium CO at a known temperature, and the nonequilibrium measurements (in which  $T_v \neq T_R$ ) must then be related to this calibration. The rotational temperature does affect band shape but to first order does not affect total band intensity. It affects band shape because under the assumption of a Boltzmann distribution in rotation (II-7, 7a, 7b) higher rotational temperatures imply molecules are stored in higher rotational states. Since the wave number of a line is proportional to

$$\Delta E = \Delta E_{v} \pm \Delta E_{R}$$

where

ΔE = energy emitted from a vibration-rotation transition of CO

- $\Delta E_v = difference of energy between two vibrational$ energy levels
- $\Delta E_R = difference of energy between two adjacent rotational energy levels$

and

$$\Delta E_{R} \sim \Delta [J (J + 1)]$$

$$\sim 2 (J + 1) \text{ (see equation (II-7a))}$$

then it can be seen that lines further out from the band origin (J = 0) are strengthened. Thus, if one were only measuring a portion of a band the emission could be quite sensitive to  $T_R$  depending on what part of the band was being observed. Such a problem was avoided in this work by using a filter and a detection system which covered the entirety of the first overtone band with fairly uniform transmission and response. Transmission functions for the two filters used, the response function of the detectors used, and the CO infrared band system can be seen in Fig. 3. To check the effect of nonuniformities in spectral response which were present in the detection systems used, the following integrals were numerically calculated for the first overtone band. \*

$$I_{1} = \int_{\text{pand}} R_{CO} (T_{v}, T_{R}, \lambda) d\lambda \quad \frac{\text{watts}}{\text{ster-particle}}$$
(II-20)

and

$$I_{2} = \int_{\text{band}} F(\lambda) D(\lambda) R_{CO} (T_{v}, T_{R}, \lambda) d\lambda . \qquad (II-21)$$

\*The author is indebted to Dr. Lee A. Young for copies of his equilibrium CO radiation computer programs which were then modified to calculate the quasi-equilibrium radiation described here.

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- $R_{CO}$  = the spectral radiation function for CO in a Boltzmann distribution in vibrational states defined by  $T_v$  and a Boltzmann distribution in rotation states defined by  $T_R$ .
- $\mathbf{F}(\lambda)$  = Percent transmission of filter as a function of wavelength.

 $D(\lambda)$  = Relative detector response as a function of  $\lambda$ .

The ratio of these two integrals was examined for  $T_v = 1400^{\circ}$ K to  $4000^{\circ}$ K and was found to vary by less than 1% when  $T_R$  was varied between  $T_v$  and  $400^{\circ}$ K; thus the effect of rotational temperature on the CO radiation measured in this experiment could be ignored, and gas emission was interpreted directly in terms of a vibrational temperature. The experimental procedure for calibration and interpretation of data will be discussed later.

A second important consequence of the band structure is that, since a band is composed of individual lines (hundreds of them), calculation of opacity of the gas (emissivity or absorptivity) at the wavelength of interest must involve a calculation of the absorptivity of individual lines even though the optical detection system used does not resolve these lines but sees them smeared together. It is important to know the opacity of the gas to be able to interpret the emission in terms of radiation per molecule. If the line radiation from the gas is of high emissivity then self-absorption by the gas itself is significant and must be accounted for. In the situation described here, it is clearly desirable to have the line radiation of low emissivity so that there is no self-absorption; then the gas will be <u>optically thin</u>, and the radiation will scale linearly with path length and concentration of radiating species at constant total pressure. If the lines were of high emissivity and optically thick (or

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black) then the radiation would not characterize the uniform gas in the center of the shock tube or nozzle, but rather that gas in the thin boundary layer adjacent to the wall.

In addition to natural broadening, the lines of a band are broadened by two additional mechanisms: (1) Lorentz or pressure broadening and (2) Doppler broadening. These two mechanisms are helpful; broadening of a line lowers the emissivity at its center (where it is most intense) by distributing the total line intensity over a larger interval of the spectrum. To calculate line emissivity one needs to know in essence the ratio of line intensity to line width. Line intensity in this case is determined by vibrational temperature, while line width is determined by pressure and translational temperature. The opacity of the first overtone of CO is determined in Appendix A by calculating the emissivity at the center of the strongest line of the band for each of the three regimes in which measurements were taken;(1) at equilibrium behind incident shock waves, (2) at equilibrium behind reflected shock waves, and (3) downstream in the nozzle where a quasi-equilibrium exists ( $T < T_{y}$ ). It is shown there that the gas is optically thin under all conditions. It was for this reason that the first overtone was used in this experiment rather than the fundamental band which is about two orders of magnitude more intense. Since there was no problem with signal to noise ratio, an added benefit was the greater sensitivity with temperature for the overtone band.

Since the gas is losing vibrational energy by radiation, it is important to know if this loss is significant. The radiative lifetime of the CO fundamental band is .033 sec and lifetimes for the overtone bands are longer. Since the flow time of the gas from equilibrium in the stagnation region to

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the nozzle exit is on the order of 100  $\mu$ sec there is no appreciable energy loss by the gas due to radiation.

The optical systems (detector, filter, and optics) used in this work were calibrated on the gas itself by measuring the radiation from hot CO behind incident shock waves in a shock tube after its relaxation to equilibrium. The gas temperature and density are very well known behind the incident shock since initial gas conditions and the shock velocity are measured. In Section III-B the apparatus will be shown and described in detail and it will be seen that the optical path geometry (path length, volume of radiating gas, window material and thickness) could be kept constant between the calibration behind incident shocks and the measurements downstream in the nozzle. The result of the calibration was to produce a plot of a quantity B which is proportional to radiation per particle per steradian vs equilibrium gas temperature. Then with a measurement of gas radiation downstream in the nozzle and a calculation of gas density at that point, this quantity B could be determined and used to enter the calibration plot and obtain a temperature. This temperature was interpreted as the vibrational temperature at that point in the nozzle and could be compared to vibrational temperatures calculated for various values of  $\phi$ . The factors necessary for this identification have been discussed in this section and are repeated here.

- The gas maintains a Boltzmann distribution among vibrational energy levels during the nozzle expansion by V-V collisions which are fast on a time scale compared to the relaxation time. Thus a vibrational temperature has meaning.
- (2) The gas is optically thin under conditions of calibration and measurements.
- (3) The effect of  $T_R \neq T_v$  has been considered and it has been

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shown that gas radiation as detected by this optical system is not affected by the value of  $T_p$ .

### C. Shock Tunnel

Shock tube and shock tunnel operation can be best understood by referring to Fig. 4 which shows an ideal wave diagram illustrating their operation. Initial conditions in the tube just before the experiment begins are high pressure driver gas (hydrogen or helium) in region 5 and carbon monoxide test gas in region 1. At time equal to zero the scored metal diaphragm at the junction of the driver and driven sections (x = 0 cm) is split open by raising the pressure in region 5 above the designed bursting pressure of the diaphragm. A shock wave propagates into region 1 producing region 2; a contact surface which separates the shocked test gas (region 2) from expanded driver gas (region 3) also propagates into the driven tube but at a lower velocity than the shock wave; and driver gas expands isentropically from region 5 through the expansion fan into region 3. A typical set of gas conditions for the various regions are also shown in Fig. 4. It can be seen that the shocked gas in region 2 is flowing toward the right at a velocity somewhat smaller than that of the shock wave and equal to that of the contact surface, since the boundary conditions across the contact surface are that the pressures and velocities of regions 2 and 3 must match. When the shock wave reaches the righthand end wall it reflects with a velocity determined by the boundary conditions that gas adjacent to the end wall must be left stationary. Conditions behind the reflected shock are labeled region 4 and form the stagnation conditions for the nozzle flow. The reflected shock, moving back up the tube, soon intercepts the contact surface and essentially

brings it to rest, although there is in general an interaction so that the reflected shock changes its velocity slightly and a wave (either compression or expansion) propagates back toward the end wall, thereby terminating the uniform conditions in the stagnation region.

In the figure shown the gas at the end wall remains undisturbed by waves for 700  $\mu$ sec. In some shock tunnels in which the nozzle is used as a short duration wind tunnel for aerodynamic testing, a longer period of uniform conditions is obtained by "tailoring" the reflected shock contact surface interaction so that no wave is reflected back to the end wall.<sup>23</sup> This is accomplished by adjustment of the sound speeds of the driver and driven gases. Despite the fact that the actual test time is considerably diminished from that shown in Fig. 4, tailoring was not used in this experiment for two reasons: (1) the maximum test time needed was only 200-300  $\mu$ sec since it was merely necessary to start the nozzle (about 100  $\mu$ sec) and establish steady flow for 100-200  $\mu$ sec and (2) the contact surface is not a line as pictured, but a diffuse layer continually growing by diffusion,<sup>24</sup> and it is the diffusion of driver gas into region 4 that eventually terminates this experiment, since the driver gas is of low molecular weight and very efficient in vibrationally relaxing CO.

Que other way the conditions in region 4 can be disturbed would be for the first reflected expansion wave (w) from the driver to propagate into region 4. It can be seen from Fig. 4 that this can be avoided simply by making the driver section long enough or by lowering the speed of sound of region 5 by the use of a different driver gas. To determine an appropriate driver length, a program was written to calculate the locus of the first expansion wave to reach the nozzle end of the shock tube used in this

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work. The solution was an exact inviscid solution by the method of characteristics for one dimensional unsteady flow<sup>\*</sup> and was actually done in reverse time order by starting with an expansion wave that just missed intercepting region 4 and solving for the driver length necessary for this wave to intercept the origin after its reflection from the left end of the driver tube. The results of this calculation are shown in Fig. 5 for the two driver gases used in this work. Since the actual driver was five feet long, hydrogen could not be used for incident shock velocities below 1.64 mm/µsec.

The wave diagram for the shock tube is somewhat modified from that shown due to boundary layer effects. Boundary layer growth 26,27 behind the incident shock is responsible for deceleration of the shock, acceleration of the contact surface and hence a reduction of the ideal value of the test time by a factor of two to four in the present case. The reflected shock interacts with this boundary layer on the walls as it moves back up the tube and a bifurcated foot is formed on the shock under certain operating conditions. The formation of this foot has been studied extensively  $2^{28-32}$ and the conditions prerequisite to its formation are known. As predicted, this foot should form for the pure CO experiments ( $M_s = 4 - 7$ ) but not in the 5% CO in Argon experiments ( $M_s = 3 - 5$ ). The effects resulting from the incident shock boundary layer which compete in determining the reflected shock velocity are: (I) the boundary condition imposed by a decelerating incident shock which tends to accelerate the reflected shock and (2) the entrainment of boundary layer gas by the reflected shock which tends to decelerate it. An additional effect is that immediately following the shock reflection there is a deceleration of the shock due to endothermic vibrational

\*See for example Shapiro, <sup>25</sup> Vol. II.

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relaxation. Dyner<sup>31</sup> maintains that these three effects may be treated separately and that experimentally he observes an initial shock deceleration due to relaxation followed by a shock acceleration as the first of the competing boundary layer effects mentioned above dominates in controlling the reflected shock velocity. In the present experiments, the time scale for the deceleration due to relaxation should be of the order of the vibrational relaxation time in the stagnation region or about a microsecond. Thus, the reflected shock is treated as an equilibrium shock and an estimate of the maximum change in stagnation conditions due to the boundary layer effects mentioned is obtained by neglecting the deceleration effect of boundary layer entrainment by the reflected shock. Such a calculation indicates that 500  $\mu$ sec (a conservative upper bound for the duration of an experiment) after its reflection, the gas temperatures and pressure are 6% and 8% higher, respectively, behind the reflected shock, than immediately after its reflection. This calculation is performed by using measured values of the incident shock velocity to give the time history of that shock and then calculating the locus of the reflected shock which must continually accelerate in order to leave the gas behind it stationary. Not only are these uncertainties tolerable, it was possible to obtain experimental verification that the stagnation temperature and pressure were within these bounds (Section III-F).

Another conceivable source of error in knowing the stagnation conditions for the nozzle flow was due to the end wall thermal boundary layer. Calculations of this boundary layer are given in Appendix B. They indicate that this thermal defect due to cooling of the gas adjacent to the end wall is negligible. An additional complication associated with this end wall boundary

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layer is its possible introduction of impurities from the wall into the flow; this matter is discussed in Section IV.

Cross sectional views of the nozzle used in this work are shown in Fig. 6 along with a plot of its area ratio (ratio of nozzle cross sectional area, perpendicular to the flow direction at some location to that area at the throat) vs distance downstream of the throat. It can be seen from this figure that the nozzle width is constant so the expansion is "two dimensional". The cross sectional area of the throat is small enough that the mass flow from the stagnation region out through the nozzle is an order of magnitude less than the rate of mass addition of gas, processed by the reflected shock, to the stagnation region. Thus, stagnation conditions and the reflected shock should not be appreciably perturbed by the nozzle flow. Referring to the wave diagram in Fig. 4, the nozzle flow starts immediately after the reflection of the incident shock wave. There is a thin diaphragm (1 mil mylar for example) which initially separates the evacuated nozzle and large dump tank into which it exhausts, from the shock tube region 1. Immediately after shock reflection, the high pressure, high temperature gas in region 4 bursts this "second diaphragm" and nozzle start-up is initiated. Nozzle start-up for an axisymmetric configuration similar to this has been studied experimentally and analytically by Smith.<sup>33</sup> Use of his results\* indicates that the time for nozzle start-up to be complete at area ratio 40 (the end of the nozzle) should be 125  $\mu$ sec or less. This figure is also roughly equivalent to a flow time for the nozzle, i.e. the time for a gas particle to flow from the stagnation region to the nozzle exit. This was observed experimentally to be true in this work, although the data presented

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A throat radius was assumed equal to that of a circle of the same area as the rectangular throat of this work.

later show times noticeably smaller than this since they were taken at area ratio 10. Because of concern with possible contamination of the flow by diaphragm material, some nozzle runs were made with the second diaphragm <u>downstream</u> of the nozzle at the junction of the nozzle with the dump tank rather than <u>upstream</u> at the junction of the nozzle with the shock tube. This arrangement completely eliminated the possibility of diaphragm material contaminating the flow. Nozzle start-up was a bit longer with this arrangement but still quite satisfactory. It should be noted that the dump tank capacity was large enough and its initial pressure low enough to keep the nozzle flowing full, with no standing shocks inside the nozzle, for over 10 milliseconds.

The boundary layers in this nozzle are small. A laminar boundary layer calculation was made for the subsonic portion of the nozzle, based on the work of Cohen and Reshotko<sup>34</sup>, and is outlined in Appendix C. The results indicate a displacement thickness of about .001 inch at the nozzle throat (throat height is .050 inch); its effect is negligible on the vibrational temperature and density predictions for the nozzle. The boundary layer in the supersonic portion of the nozzle was calculated using the results of Burke.<sup>35</sup> He studied the boundary layer in the supersonic portion of a shock tunnel under conditions similar to those of this work and found it to be turbulent. He correlated his results and gave semi-empirical relations for the displacement thickness which include Mach number and Reynolds number dependence. In the present experiment, the ratio of stagnation to nozzle pressure was measured for area ratio 15, and the results were in agreement with the predicted value of the displacement thickness to within a factor of two. A factor of two uncertainty in the displacement thickness has a

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negligible effect on the vibrational temperature, and a small effect on the density predictions for area ratio 10 in the nozzle where most data were taken. The effect of this uncertainty in the density on the values of  $\phi$  obtained in this work will be considered quantitatively in Section IV.

The nature of the non-equilibrium flow in the nozzle can be seen in Fig. 7. In the case shown, it can be seen that the vibrational temperature of the gas follows the translational temperature, staying nearly in equilibrium un'il area ratio 2, at which point it "freezes out" and remains constant thereafter. This rapid freezing behavior is typical of gas relaxation in supersonic nozzle flows; it was first observed by Bray<sup>36</sup> in calculations of three-body recombination in a nozzle flow. It occurs in the present case because of the steep temperature dependence of the vibrational relaxation time, coupled with the rapid temperature drop and increase in gas velocity as the gas flows down the nozzle. Initially the temperature is high, making the relaxation time very small, and the velocity is low, implying the time rate of change of temperature is small for gas particles moving down the nozzle; thus, the vibrational temperature remains in equilibrium with the gas temperature. However, as the gas temperature drops, the relaxation time increases rapidly due to its exponential temperature dependence (equation II-18) until the vibrational temperature begins to lag in its attempt to match the gas temperature. Meanwhile the gas continues to accelerate, increasing the time rate of change of gas temperature and thereby compounding the effect; the result is rapid freezing of vibrational energy and frozen flow from that point on in the nozzle. Thus the vibrational temperatures measured at area ratio 10 and larger are frozen at some point earlier in the nozzle and are no longer changing.

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Because measurements in this work are only obtained after freezing has occurred, there are limitations to possible interpretations. Since the rapid freezing model is qualitatively correct, one is only certain of the value of  $\phi$  at the freezing temperature. Upstream of the point where freezing occurs, the temperature is higher, the flow is essentially in equilibrium, and  $\phi$  may be infinite without changing the results; downstream where the temperature is lower, the vibrational energy is frozen, and  $\phi$  may be one or even zero without affecting the results. This assumption of a constant value of  $\phi$  has these limitations, but with no more detail about the relaxation in the non-equilibrium region where freezing is occurring there is no justification for a more sophisticated approach.

The calculation of stagnation conditions behind the reflected shock was performed using a frozen-incident/equilibrium-reflected shock model. For calculation of conditions adjacent to the end wall this model is reasonable because near the end wall the gas behind the incident shock has not vibrationally relaxed before the reflected shock propagates into it and yet the relaxation time behind the reflected shock is so short that it essentially propagates as an equilibrium shock. Closed form solution of the equations for this model is not possible owing to the exponential temperature dependence in  $\overline{\sigma}$ , so an iterative solution was programmed.<sup>\*</sup> Calculations were performed for pure CO, and for mixtures of CO-argon and CO-H<sub>2</sub>-H. The CO with hydrogen calculations were the most complicated, since there were three gas components and the term "equilibrium reflected shock" in

\*All programming was done in Fortran IV for solution on an IBM 360/44 digital computer.

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this case implied equilibrium CO and  $H_2$  vibrational energy and equilibrium  $H_2 \rightarrow 2H$  dissociation; the solution for this case is outlined in Appendix D. Equilibrium incident shock calculations were also performed to obtain the gas conditions used in the incident shock calibrations. Some results of these various shock calculations are presented in Figs. 8-10. These calculations are all presented vs incident shock velocity because this was the independent variable in the experiments; one initial shock tube pressure ( $P_1 = 4 \text{ ch}$  for pure CO experiments) and temperature ( $T_1 = 294^{\circ}$ K in all calculation's) was used for a series of experiments; thus all data were correlated with the measured incident shock velocity. Incident shock velocity was controlled by changing the diaphragm bursting pressure ( $P_5$ ).

The calculations of the steady state nozzle flow was performed in a manner similar to that of Stollery and Smith. <sup>37</sup> In this work the Bethe-Teller relaxation equation (II-14) for the local vibrational energy  $\sigma$  was numerically integrated from the stagnation region down the nozzle. In this integration the equilibrium vibrational energy  $\overline{\sigma}$ , and the relaxation time  $\tau$  (p, T,  $\phi$ ), are evaluated locally from those values of p and T given by a one-dimensional equilibrium solution of the nozzle flow for specified stagnation conditions. Simultaneously, the entropy gain due to the transfer of energy from vibration at temperature T<sub>v</sub>, to translation at temperature T was calculated by:

$$S_{o}(x) = S_{o}(o) + \int_{o}^{x} \frac{d\sigma}{dx} \left(\frac{1}{T_{v}} - \frac{1}{T}\right) dx \qquad (II-22)$$

So(0) = entropy in the stagnation region erg/gm-<sup>0</sup>K
So(x) = entropy at any point x in the nozzle downstream
from the stagnation region.

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The equilibrium solution was then "corrected" by resolving the equations for equilibrium flow with the modification that: (1) instead of using  $\overline{\sigma}$  in the energy equation, the vibrational energy distribution just obtained is used to specify  $\sigma$  at each point in the nozzle and (2) the entropy is allowed to increase according to equation (II-22). The advantage of this method is that it avoids the saddle point singularity at the throat of an exact one-dimensional integration of the nozzle flow equations.

To the point of finding the vibrational energy (and thus the vibrational temperature) by integration of the Bethe-Teller equation, as described here, this method is identical to that of Stollery and Smith. This method has been used by other investigators<sup>5</sup> and has been shown by Stollery and Park<sup>38</sup> to give good agreement with exact one dimensional calculations. The method used here to correct the equilibrium solution is slightly different from Stollery and Smith, in that the entropy function was integrated rather than the Euler equation. It can be seen from equation (II-22) that the entropy gain depends on the rapidity of the freezing process in the nozzle. If the gas follows equilibrium exactly and then freezes instantly at some point in the nozzle, then there is no entropy gain since  $T_v = T$  during the equilibrium phase and  $\frac{d\sigma}{dx} = 0$  for the frozen portion of the flow.

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## III. EXPERIMENTAL HARDWARE AND TECHNIQUE

## A. Shock Tunnel

A schematic layout of the shock tunnel and its associated components is shown in Fig. 11; the nozzle end of the tube and the gas handling manifold are shown in the photographs of Figs. 12 and 13. The shock tube driver and driven sections up to the transition section are stainless steel pipes of 1.5-inch-inside-diameter and five-foot-length; sections are bolted together through flanges welded to their outer circumferences, aligned through guide pins and sockets in these flanges, and vacuum sealed by rubber O-rings coated with vacuum grease. The transition section is 10 inches long and provides a smooth transition at constant area from 1.5-inch-inside-diameter round cross section to a 1.33-inch-square cross The remainder of the shock tube up to the nozzle entrance consists section. of 1, 33-inch-square extruded aluminum sections joined in the same manner as the other sections. Two square sections were used to allow the use of flat windows to view the stagnation region at the end of the shock tube. The shock tube is supported on carriages which roll on tracks bolted to the floor; this allows easy access and disassembly of the tube at any of its joints. At the junction of the driver and driven sections there is a provision for mounting, and sealing with O-rings, a metal diaphragm. This diaphragm is scribed in its center with two saw cuts at right angles to each other, which allow it to open into four petals at a predetermined pressure differential across it. In the driven tube, 0.875 inches from the junction of this tube with the nozzle, there are two openings in which either a window holder or a pressure gage holder may be mounted with an O-ring seal; identical openings and mountings are found in the nozzle block. The nozzle block is

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constructed of stainless steel with the nozzle contour shaped from brass pieces which fit inside the steel shell. The nozzle is joined to both the shock tube and the dump tank with bolted flanges and dual concentric O-ring seals. The second diaphragm is held in place by the O-ring seals at either of these two junctions.

The gas handling manifold system is shown schematically in Fig. 11 and in the photograph in Fig. 13. The carbon monoxide is introduced from its storage cylinder through a Matheson carbon monoxide pressure regulator and copper lines to the filter shown in the schematic. This filter consists of a 10 foot copper coil filled with alumina held in a dry ice-acetone filled dewar followed by another 10 foot copper coil filled with copper wool and held in a liquid nitrogen filled dewar. The reasons for this filter are disquessed in the later section on gas purity. Other gases which were used in making gas mixtures are introduced directly into the stainless steel mixing tank. Also attached to the manifold at various points are the pressure measuring instruments and gauges and the pumps.

Separate mechanical pumps (five cubic feet per minute) are used in evacuating the driver tube, the driven tube, the dump tank, and on the exhaust of the diffusion pump. The driven tube, manifolding, filter, mixing tank, and all lines and regulators up to the main valve on the gas supply cylinders are evacuated with a four inch oil diffusion pump with a liquid nitrogen cooled baffle at its junction to the system. The driven tube, manifolding, and filter are evacuated typically to 0.  $0l\mu$  with a leak-plusoutgassing-rate of  $0.2\mu$ /minute when the pumps are closed off from the system. This vacuum and leak rate are important in maintaining the purity of the CO once it is introduced into the system from its storage cylinder.

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Vacuum and leak rates are measured with National Research Corporation Alphatron (1 atm -  $1\mu$  Hg) and ion  $(5\mu - 10^{-4}\mu)$  gauges. Gas pressures for making mixtures and initial test gas pressure ( $P_1$ ) are measured on a Bourdon gauge (0 - 100 psi), a mercury manometer (0-24 cm), a butyl phthalate manometer (0-10 mm Hg), or a McLeod gauge (10 mm -0.  $01\mu$ ). A liquid nitrogen trap was used between the manifold and manometers as shown in Fig. 11 to prevent mercury outgassing into the system, except in those cases when some constituent of the gas mixture being used would trap out and thereby lead to an erroneous pressure measurement.

Two Kistler (models 603A and 606L) piezoelectric pressure transducers and charge amplifiers (model 504) were used to measure pressure in the stagnation region and downstream in the nozzle during shock tunnel operation. Such measurements were useful for determining the timing of certain events such as shock arrival and reflection, the duration of steady conditions in the stagnation region, arrival of waves from the reflected shock, contact surface interaction, and the duration of nozzle start up. They also gave quantitative pressure measurements and, thus, could be used to determine boundary layer displacement thickness in the nozzle. These gauges were supplied from the manufacturer with calibration charts; however an additional check on their calibration was easily obtainable by measuring the pressure behind incident shock waves. Results of these measurements are shown in Fig. 14 and indicate good agreement between pressures measured and those calculated on the basis of the initial gas conditions and the measured shock velocity.

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The level of these measured pressures is higher than that of the pressures in the nozzle and lower than in the stagnation region; however these quartz piezoelectric gauges are linear over the several decades for which they were calibrated according to the calibration charts supplied by the manufacturer. Although rise time of these gauges was quoted by the manufacturer as 1  $\mu$ sec, a resonant ring of 10  $\mu$ sec period was present and particularly noticeable in the low pressure measurements in the nozzle. In these latter measurements oscillations with an amplitude on the order of the average signal were present thereby leading to some uncertainties in the absolute signal level.

The shock velocity was measured during a run by means of four thin film, platinum heat transfer gauges placed at measured intervals along the shock tube. The hot gas behind the incident shock would cause the platinum resistance to change. The platinum element, being one leg of a bridge circuit, generates a voltage change which was then amplified and displayed on a folded oscilloscope (Tektronix model 535) sweep along with signals generated every 10  $\mu$ sec by a time marker (Radionics Inc. triangle and marker timing generator). Figure 15 shows the locations of the four gauges used for this measurement along with an oscillogram showing the signals from these gauges. A calculation of the average shock velocity between the different gauges is also shown. In the experiments, the three values of velocity were plotted vs their average shock tube coordinate for the interval of the measurement, and a curve drawn through these points was extrapolated to the location of the end wall or nozzle entrance. The velocity at that point was taken as the incident shock velocity at the moment of reflection and data were correlated with it. A fifth gauge, which is not illustrated, was

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located between gauge  $H_1$  and the driver tube and was used to trigger the oscilloscope sweep. The last gauge( $H_4$ ) was used to trigger the oscilloscopes (Tektronix model 555) on which data from the nozzle and stagnation region were recorded.

## B. Optical System

The optical system is shown schematically in Fig. 16 and can be seen in the photographs of Figs. 12 and 17. There are two essentially identical systems, one on each side of the shock tunnel. Each system is mounted on a small carriage, which can be seen in Fig. 12, and which rolls parallel to the shock tube, so that a system can be quickly aligned with any of several windows in the nozzle or stagnation region. This configuration allowed preserving the optical path geometry between calibration and measurement, a feature that was not necessary but definitely convenient.

The optical system consists simply of a spherical mirror, used to give unit magnification of the detector element into the center of the shock tube or nozzle, a flat mirror, an interference filter to provide the desired infrared band pass, and a liquid nitrogen cooled indium antimonide detector (Philco ISC-301C & D). This configuration is mounted in a rigid aluminum frame painted with flat black lacquer which was found to be a poor reflector at 2. 3 $\mu$ . All windows used in the shock tube and nozzle were 0. 080-inchthick sapphire. The transmission of these windows was measured on a spectrometer and found to be constant at 88% from 1. 5 $\mu$  to 4 $\mu$ . The f-number of the system is controlled by an aperture held immediately in front of the spherical mirror. Care was taken in designing the system so that <u>no</u> light would be restricted by apertures other than this, such as the window holders or the shield around the detector. The area of this aperture opening (A<sub>m</sub>)

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can be used to control the magnitude of the signal reaching the detector and thereby keep it operating in a range where it is linear and has been calibrated. The detector is photovoltaic and its output in parallel with a load resistor is fed directly to the oscilloscope preamplifier (Tektronix model 1A7). The load resistor was adjusted for maximum signal; this occurred around 500 ohms. The signal-to-noise ratio in most cases was excellent, being typically about 100. The rise times of the detectors and the preamplifiers were given by their manufacturers as being about 1  $\mu$ sec, and 0.  $3\mu$ sec, respectively. In the measurements behind incident shock waves the resolution time of the optical system was several  $\mu$ sec since shock velocities were 1 to 2 mm/ $\mu$ sec and the detector element (which is imaged in the shock tube) is 1 or 2 mm in the direction of the flow depending on the detector.

Initially a precursor of radiation was observed in the calibration runs behind incident shock waves indicating that radiation was reaching the detector before arrival of the shock wave. The source of this radiation was found to be radiation scattered in the manner shown by ray 1 in Fig. 18; it was easily eliminated by painting the scattering surface black. Another source of stray radiation considered was that which could arrive by multiple reflection as shown by ray 2 in Fig. 18. Radiation arriving in this fashion must pass through the detector image d' and within the solid angle  $\Omega$ . In the calibration this was not possible because another window (a poor reflector) was positioned opposite the viewing window; however in the nozzle the brass side wall was opposite a viewing window and thus a systematic error could result between the calibration and the measurements. To check this possibility a dummy window was made of solid brass and placed in the shock tube opposite an optical system for measurements of radiation behind

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incident shocks. A definite increase in radiation was observed with this arrangement. However, it was found that when the brass window was painted with black lacquer or covered with black masking tape there was no increase in radiation compared to that recorded when a window or a lucite plug was opposite the optical system. Thus black tape was placed on the wall opposite a viewing window in the nozzle.

A black body radiation source (Barnes Engineering model 11-201) and mechanical chopper wheel were used to determine the range of linear operation of the detectors. For the black body at a fixed temperature, the mirror aperture in the optical system was varied; a plot of signal divided by mirror area vs signal revealed at what signal level saturation for the detector occurred. A program was also written to compute the integral I<sub>2</sub>.

$$I_{3} = \int F(\lambda) D(\lambda) \stackrel{o}{R}(T, \lambda) d\lambda$$
(III-1)'  
filter  
bandpass

 $\stackrel{o}{R}(T,\lambda) = black body spectral radiation function in <math>\frac{erg}{sec-cm^2-steradian}$ 

 $F(\lambda)$  = spectral transmission function of filter in percentage

 $D(\lambda)$  = spectral response of detector in percentage

Then by varying the black body temperature, detector response vs  $I_3$  was checked for linearity. Using both of these methods together it was possible to determine that the detectors responded linearly with radiated power from 10  $\mu$ v (near the noise level) to 10 millivolts where saturation began.

In considering radiation that could be detected by the optical systems, it is important to remember that the fundamental band is up to two orders of magnitude more intense than the first overtone band of CO at  $1500^{\circ}$ K (a lower limit for the vibrational temperatures measured in this work) and above. Since the detector response is approximately equal for each of these bands it is important that the filter transmission be very small in the wavelength region of the fundamental. To examine this, the filter transmission functions were measured with a Perkin Elmer model 21 dual beam infrared spectrometer and found to be less than 0.1% for wavelengths longer than 4.  $3\mu$  (location of the band head for the fundamental band). This figure represents the limit of sensitivity for that instrument but still assures that, for the radiation detected, less than 10% of the total signal can come from the fundamental.

# C. Gas Purity

An important aspect of any measurement of vibrational relaxation times is the purity of the gas. Several bottles<sup>\*</sup> of gas were purchased for these experiments and analyzed for impurity content. These samples were initially scanned for absorption spectra in the infrared from  $2\mu$  to  $10\mu$  in a one meter, one atmosphere cell on a Perkin Elmer model 21 spectrometer. All of the samples passed this initial screening for infrared active impurities. Then samples of the gases were sent off for mass spectrometer analysis;<sup>\*\*</sup> some results are shown in Table I. The Matheson research grade gas was supplied by the manufacturer with an analysis; these results are also given in Table 1. Unfortunately this gas was not as pure as their analysis indicated

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C.P. grade from General Dynamics and Matheson, and research grade from Matheson and Linde

<sup>\*\*</sup>Gollob Analytical Service, Berkley Heights, N. J.

and some additional purification was necessary to remove the nickel carbonyl and possible propane. This purification was achieved by a simple trap system given by Millikan<sup>39</sup> and described earlier in this paper under Section III-A. The beneficial results of this additional purification can be seen in the mass spectrometer analysis. Further, a definite improvement (decrease of  $\phi$ toward 1) in the nozzle measurements was observed when the gas was purified in this manner. \* After filtering, the General Dynamics and the Matheson research grade gases gave identical results in the nozzle measurements.

Additional confirmation on the purity of the CO was obtained by measuring the relaxation time behind incident and reflected shock waves. These measurements were performed in the course of the optical system calibration and study of the stagnation region behind the reflected shock. The results of the measurements are shown in Fig. 19 where they are compared to the equation of Hooker and Millikan<sup>12</sup> which fits their data and that of Matthews.<sup>13</sup> The gas used in these measurements was the General Dynamics C. P. grade without further purification. The agreement of this data with that of Hooker and Millikan, who exercised considerable care with their gas purity, was felt to be sufficiently close as to not warrant further measurements of relaxation time when the benefits of additional filtering were later found.

For the range of stagnation conditions covered in this work the dissociation energy of CO is sufficiently high that no appreciable dissociation can occur in the stagnation region. Figure 20 shows the degree of CO dissociation vs the range of incident shock velocities used in the nozzle flow experiments.

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<sup>&</sup>lt;sup>\*</sup>Radiation intensity from measurements in the equilibrium region behind incident and reflected shock waves was unaffected by the choice of gas sample or by additional purification.

### D. Operation

The usual sequence of operations involved in making a nozzle run is as follows.

- (1) Install the two diaphragms, seal the tube and pump on the three parts of the shock tunnel with their individual roughing pumps. These three parts are: (a) driver section, (b) driven section, manifolding, filter and gas lines up to the pressure regulator on the gas cylinder, and all pressure measuring instruments and gauges, and (c) dump tank and nozzle.
- (2) Upon reaching  $200\mu$  pressure in part (b) the roughing pump is closed off and the diffusion pump opened. Pumping continues until a pressure of about 0.  $01\mu$  and a leak plus outgassing rate of about 0.  $2\mu/\text{min.}$  are reached; this requires around 20 to 30 minutes.
- (3) Adjust oscilloscope gain settings and sweep rates and set the oscilloscopes for a single sweep trace.
- (4) Pour liquid nitrogen into the dewars on the detectors.
- (5) Close off all pumps to all parts of the shock tube.
- (6) Measure the test gas into part (b) at pressure  $P_1$ .
- (7) Close off the shock tube driven section from the manifold.
- (8) Turn on the bias voltage to the heat transfer gauges and open the shutters of the Polaroid cameras on the oscilloscopes.
- (9) Measure gas into the driver section until the diaphragm splits.
- (10) Develop oscillograms, turn off bias voltage, pump out parts (a), (b), and (c) with the driver section roughing pump exhausting to the roof.

(11) Upon reaching 1 mm pressure close off the pump, open the tube to the room and begin step (1).

Steps (1) through (11) require about 40 minutes while steps (5) through (9), which are important for preventing gas contamination by outgassing from the tube walls, require about 2 minutes. Optical system alignment and oscilloscope calibration were checked each morning. The entire optical system was checked periodically with a black body for comparison with previous measurements to ascertain any loss of sensitivity with time -- none was ever observed.

### E. Data Analysis

Figure 21 shows raw experimental data for nozzle runs. The lower traces on Fig. 21 (b) and (c) show pressure measurements in the stagnation region. The pressure gauge was 0.24 inches-diameter and centered at a location 0.875 inches from the end wall or nozzle entrance. The first step on this signal, which lasts for about 50  $\mu$ sec, measures the pressure behind the incident shock and the time required for the shock wave to reach the end wall and to return to this location. The second rise in the signal marks the arrival of the reflected shock as it moves back up the tube. There is a clear distinction between the two traces shown due to the bifurcated foot on the shock in pure CO. The presence of this foot in the one case (c) and not the other is expected on the basis of criteria for its formation given by Mark<sup>28,29</sup> and others. <sup>40</sup> The pressure then climbs gradually, probably due to reflected shock acceleration mentioned earlier, and then begins to climb more steeply as waves from the interaction of the reflected shock with the diffuse contact surface arrive in the stagnation region. The later falling of the pressure in the pure CO experiment may be due to arrival of expansion waves from the driver.

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Similar features can be seen in the CO first overtone emission shown in Fig. 21(a). In that trace the emission level which is relatively constant for 200 µsec at the center of the picture is interpreted in terms of the stagnation gas temperature. First overtone emission downstream in the nozzle is also shown in Fig. 21. In (a) and (b) there is a spike at the beginning of the signal due to some (unknown) emission from the residual air in the nozzle as the primary shock and secondary shock pass by the viewing window. \* This feature is quickly damped as expansion waves complete the nozzle start up. The start up is more prolonged further down the nozzle at area ratio 35 (see top trace Fig. 21(b)), since all the starting waves originate simultaneously near the nozzle throat and move at different velocities down the nozzle. These traces then drop off abruptly after 200 to 300 µsec quite probably due to diffusion of some driver gas into the stagnation region. This occurs earlier in the case of the pure CO because test times are shorter than in CO-argon mixtures since higher shock velocities are needed to produce similar stagnation temperatures. The signal amplitude was read at the earliest point where it seemed to level off or begin to turn upward; thus in general it was read at the lowest point on that portion of the trace before driver gases began to modify the CO relaxation. These infrared emission signals were interpreted in terms of a vibrational temperature.

Some data illustrating CO first overtone emission behind incident and reflected shock waves are shown in Fig. 22. These data were used to measure the CO relaxation time which was shown in Fig. 19 and to calibrate the infrared optical systems. The signals can be seen to rise in an exponential manner

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<sup>&</sup>lt;sup>\*</sup>See "The Starting Process in a Hypersonic Nozzle" by C. E. Smith <sup>33</sup> for a more detailed account of nozzle start up.

to an equilibrium level; the later rise in the reflected shock trace is due to compression waves from the reflected shock/contact surface interaction. In the interpretation of relaxation times from such data it must be remembered that overtone emission results mainly from  $v = 2 \rightarrow 0$  radiative transitions and that the collisional excitation of molecules into the v = 2 level is via a two step,  $v = 0 \rightarrow 1 \rightarrow 2$  process, rather than the direct  $v = 0 \rightarrow 2$  excitation. This was first suggested by Windsor, Davidson, and Taylor<sup>14</sup>, <sup>41</sup> and later confirmed by Hooker and Millikan.<sup>12</sup> The proper interpretation of first overtone emission for determining the relaxation time as defined in equation (II-13) was given by Decius.<sup>18</sup> Assuming the radiation from the unrelaxed gas is negligible, we have

$$\frac{\mathrm{I}}{\mathrm{I}_{\mathrm{e}}} = \left\{ 1 - \mathrm{e}^{-\mathrm{t}/\tau} \right\}^2 \tag{III-2}$$

I = first overtone emission

 $I_e = emission at equilibrium after the relaxation$ thus at  $t = \tau$ ,  $I/I_e = (1 - e^{-1})^2 \approx 0.4$ . Relaxation times shown on Fig. 19 were found by measuring the time for signals (as in Fig. 22) to reach 40% of their equilibrium values. For incident shock measurements it was also necessary to convert from laboratory time to gas particle time since the relaxing gas is flowing past the measuring device. These times are related by

$$\tau_{\text{particle}} = \tau_{\text{lab}} \cdot \frac{u_1}{u_2} = \tau_{\text{lab}} \cdot \frac{\rho_2}{\rho_1}$$
 (III-3)

where  $\rho_1$ ,  $\rho_2$ ,  $u_1$ , and  $u_2$  are the gas densities and velocities before and after the incident shock in coordinates fixed to the shock wave. The relaxation times are correlated in Fig. 19 with temperatures obtained from equilibrium incident shock solutions (Fig. 8).

## F. Calibration

The calibration of the two optical systems was performed on the gas itself by measuring the equilibrium radiation from CO behind incident shock waves. To perform the calibration it was merely necessary to replace the nozzle with an additional section of square shock tube and use the windows which normally view the stagnation region for a nozzle run; in this manner the optical path geometry remains unchanged for all measurements. Since the gas is optically thin and all geometrical factors remain constant the radiation detected is proportional to gas density and the solid angle into which gas particles can radiate and be seen by the detector. The gas density is determined by Fig. 8, and the relevant solid angle is just  $A_m$  divided by the distance from the center of the shock tube to the spherical mirror in the optical system. The quantity

$$B = \frac{S}{A_m n_{CO}}$$
(III-4)

where S = radiation signal from the detector in millivolts deflection on the oscilloscope

 $A_m = \text{area of mirror aperture in the optical system in cm}^2$  $n_{CO} = \text{number density of CO in particles/cm}^3$ 

is then linearly proportional to radiated power per particle per steradian. The calibration plot for an optical system thus consisted of a plot of B vs equilibrium gas temperature behind incident shocks. Such a plot for one of the optical systems is shown in Fig. 23. The curve which is drawn through the data was obtained by plotting the integral  $I_2$  vs  $T_v$  (see equation II-21) on an identical sheet of semi-log graph paper and adjusting this curve to give a best fit with the data. Since  $I_2$  and B are related by a constant, they both should have the same temperature dependence. The fact that the temperature dependence of the data matches that of the theory indicates that the system is measuring just the first overtone emission of CO without extraneous radiation from the CO fundamental (which has noticeably less steep temperature dependence) or other sources. The sensitivity to temperature is obvious from this plot -- for instance, a  $100^{\circ}$  change in temperature at T =  $3000^{\circ}$  produces a 10% change in signal.

Analysis of the data taken in the nozzle or in the stagnation region then simply required calculating the parameter B for any measurement, entering the calibration plot, reading off the corresponding temperature, which was interpreted as the vibrational temperature, and comparing it to the vibrational temperatures calculated with various values of  $\phi$  for that run. To form the parameter B for a run it is necessary to calculate the gas density for that measurement. Since density in the nozzle is also a function of  $\phi$ , the procedure should be iterated. There was no need for this however, because the data in a given set of experiments all fell near one value of  $\phi$ ; so the density calculations for just that value of  $\phi$  could be used.

Data for nozzle runs are presented in the next section in two ways. The experimentally determined parameter  $S/A_m$  is plotted vs incident shock velocity along with theoretical curves for specified values of  $\phi$ . These theoretical curves are determined from calculated values of  $T_v$  and  $n_{CO}$  for a particular area ratio and a calibration curve (such as Fig. 23). Data are also reduced to vibrational temperatures and plotted along with theoretical curves of  $T_v$  vs incident shock velocities. Additional abscisse on these plots relate the shock velocity to stagnation conditions.

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Measurements were also taken to confirm the calculated stagnation conditions. Pressure and vibrational temperatures were measured in the stagnation region at a location 0.875 inches from the end wall or nozzle entrance. Measurements were obtained with an aluminum plate blocking the nozzle entrance and with the nozzle in operation. Further measurements were taken with an adjustable plug inserted in the end of the shock tube as shown in Fig. 18; this arrangement allowed focusing of the optical system adjacent to the end wall. It is to be noted that for incident shock velocities above 1.75 mm/ $\mu$ sec the vibrational relaxation time is less than 1  $\mu$ sec and thus for the time scale of these measurements the vibrational temperature follows the translational temperature. Results of these measurements are shown in Figs. 24 and 25. The measured stagnation pressures and temperatures indicate good agreement with calculated values and no appreciable perturbation on these conditions with the nozzle operating. Figure 25 indicates that the stagnation temperature is not affected by nozzle operation.

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### IV. EXPERIMENTAL RESULTS

Figure 26 shows results of measurements taken at area ratio of 10 in the General Dynamics C. P. grade and Matheson research grade CO after filtering. The data show  $\phi \simeq 5$  for nozzle freezing temperatures around 2000° - 2500°K, thereby indicating vibrational relaxation in this nozzle expansion to be about five times faster than behind shock waves. At the lower shock velocities resolution in  $\phi$  is lost and it is impossible to discern between  $\phi = 5$  and  $\phi = 1$ . The dashed line in this figure gives the throat temperature for equilibrium flow and can be used to indicate whether vibrational energy freezing is occurring upstream or downstream of the throat. It can be seen that as the stagnation temperature and pressure go up, the freezing point moves further down the nozzle.

The first result obtained in this experiment for the C. P. grade gas was  $\phi \simeq 10$  at all shock velocities, and for the research grade gas  $\phi = 10$ was obtained for  $U_g = 1.7 \text{ mm/}\mu\text{sec}$  and above with a tapering off to  $\phi = 50$ at lower shock velocities. The carbonyl and propane impurities in the research grade gas (see Table 1) were suspected for the different behavior of that gas at lower shock velocities. To investigate this explanation the dual trap filter described earlier was installed in the system. The result of its use was not only to eliminate the  $\phi = 50$  result at low shock velocities but to move the results at higher shock velocities to  $\phi = 5$ . When the C. P. grade gas was again tried it, too, gave  $\phi = 5$  under all conditions. Reanalysis of the C. P. grade gas after filtering indicated a decrease of CO<sub>2</sub> content from 730 ppm to 41 ppm. To see if this difference in CO<sub>2</sub> content could have been responsible for the earlier  $\phi = 10$  result and to determine possible effects from the current CO<sub>2</sub> content, runs were made with 1000 ppm of CO<sub>2</sub>

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added to the filtered gas; this produced no change from the  $\phi = 5$  results. One possible explanation for the improvement of the C. P. grade gas with filtering would be an initial concentration of some high molecular weight species such as a hydrocarbon which could not be detected in the mass spectrometer analysis but would trap out at liquid nitrogen temperature. The molecular oxygen which appeared in the analysis was also considered for its possible effect on the relaxation. Runs were made with 1000 ppm of  $O_2$ added to the purified C. P. grade CO and no change from the  $\phi = 5$  results was observed.

The level of impurity with which we need be concerned in this experiment can be estimated by the use of Fig. 27 in which the lowest curve shows the probability (P10) for vibrational de-excitation of pure CO. This curve is obtained by converting the relaxation times of Hooker and Millikan<sup>12</sup> to probabilities by use of equations (II-15) - (II-18). The gas kinetic cross section required for the collision frequency was taken from Hirschfelder, Curtiss and Bird. <sup>42</sup> In the range 2000°K - 2400°K, where the measurements in this experiment give information on the relaxation, it can be seen that  $P_{10} \simeq 10^{-5}$ . Thus it is unlikely that any impurity in concentration of less than I part in 10<sup>5</sup> or 10 ppm could affect the relaxation unless it were to dissociate behind the reflected shock and thereby multiply its importance. This estimate is based on the impurity having a gas kinetic cross section similar to that of CO and a probability of one for de-excitation of CO. Since the mass spectrometer has a threshold for detection of 4 ppm for most species it is felt that the gas used in these experiments has no unknown impurities of mass less than 100 atomic mass units which could be affecting the results.

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The other possible source of impurity in these experiments is that which comes from the shock tube and gas handling manifold. The simplest way in which this can occur is for contamination of the test gas from normal leakage plus outgassing to occur between the time it is measured into the system and the diaphragm is broken. Since this time is about two minutes, the leak plus outgassing rate is only  $0.2 \mu$ /minute, and the initial test gas pressure is 4 cm, the contamination from leakage plus outgassing is only about 10 ppm. This figure would seem too low to be of importance, particularly since several runs were made in which the time between loading the test gas and breaking the diaphragm was extended to thirty minutes with no effect on the results.

Another possibility is for impurity to be "boiled" from the shock tube walls by the hot gas in the stagnation region behind the reflected shock; this is a difficult possibility to investigate. The only thing which was done experimentally to shed light on this question was to vary the initial pressure in the experiment. If one hypothesizes that the release of impurity from the wall is suppressed by increasing pressure or even if the impurity number density remains constant, then one expects  $\phi$  to decrease toward one as pressure is increased because the fraction of the total gas that the impurity represents would become smaller. This hypothesis is plausible since the end wall boundary layer thickness varies inversely as the square root of pressure. However the situation is actually more complicated since the heat transfer to the wall increases in proportion to the square root of a pressure increase and nothing is known about what impurity we are concerned with nor the mechanism for its release. It has been shown in Appendix B that the

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end wall boundary layer is of negligible thermal importance; what is stressed here is the possible introduction of impurities from the wall through the mechanism of this boundary layer. These impurities could wield leverage in affecting the relaxation that far exceeds any importance suggested by their mass fraction of the flow.

The results of measurements at different initial pressures are shown in Fig. 28 and are summarized in Fig. 29. In this latter figure the X-points were calculated under the assumption that the  $\phi = 5$  result at  $P_1 = 4$  cm is due to impurity from the wall and that the number density of this impurity remains constant as initial CO pressure is changed; this calculation is outlined in Appendix E. Under this hypothesis it appears from Fig. 29 that if there are effects caused by impurity from the wall, they are saturated out for initial pressures of  $P_1 = 4$  cm and higher.

The possibility of contamination of the flow with diaphragm material from the "second diaphragm" (see Fig. 11) was considered. To examine this many runs were made with that diaphragm downstream of the nozzle at the junction of the nozzle with the dump tank. No difference in vibrational temperatures measured in the nozzle could be attributed to diaphragm material. Occasionally erratic spikes and dips in the radiation signal would be observed on a run with the diaphragm upstream, but never when it was downstream.

Measurements were also made of the vibrational relaxation of CO in a mixture of 5% CO + 95% Ar in order that a direct comparison could be made with other investigators who have used this mixture; a mass spectrometer analysis of the argon used is given in Table 1. Figures 30 and 31 show these data which can be seen to scatter from  $\phi = 1$  to 5. Within the scatter of these

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data it is not possible to assert that  $\phi$  is any different from unity. The fact that this mixture gives, on the average,  $\phi$  closer to one than does pure CO and indeed gives  $\phi = 1$  for a number of runs, is puzzling. One plausible explanation is that the CO has some impurity of mass greater than 100 (and hence not detected in the mass spectrometer analysis) which is not present in the argon. In such a case, mixing 5% CO in argon would dilute any impurity in the CO by a factor of 20. Thus, despite the fact that argon is only about 1/4 as efficient as CO in relaxing CO, it is shown in Appendix F that one can expect to see  $\phi \sim 1.5$  in the mixture if  $\phi = 5$ in the 100% CO is due to impurity in the CO.

For the data shown in Fig. 31, the measurements were taken at area ratio 35. These results indicate that the vibrational temperatures does remain frozen during this further expansion.

At one point in the course of this investigation, it was suspected that one of the gas samples had a trace amount of molecular hydrogen. To investigate the possible effects of this, runs were made with various amounts of  $H_2$  added to the suspected gas. The effect of the hydrogen on the results was dramatic; the addition of 250 ppm of  $H_2$  doubled the value of  $\phi$ measured. This result was far larger than would be indicated by a calculation of the effect of  $H_2$  on the relaxation of CO, using measured relaxation times. <sup>12</sup> The explanation was traced to the presence of hydrogen atoms. This can be clearly seen by comparing the equilibrium degree of hydrogen dissociation in the stagnation region shown in Fig. 32 with measurements in the nozzle for 1%  $H_2$  + 99% CO, as shown in Fig. 33. The rapid increase in  $\phi$ 

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<sup>&</sup>lt;sup>\*</sup>Argon is apparently produced in a quite pure state since the lowest grade commercially available is generally rated as 99.995% pure.

beginning around shock velocity 1.5 mm/ $\mu$ sec is seen to correlate with the rapid increase in H-atom concentration from roughly 2 parts in 10<sup>4</sup> at this velocity to full dissociation or 2 parts in 10<sup>2</sup> at the highest shock velocities. Results for other amounts of molecular hydrogen in the initial gas are also shown in Fig. 33. When these runs were performed the "pure CO" was giving results closer to  $\phi = 6-8$  rather than  $\phi \leq 5$  as shown earlier. These two sets of data for pure CO lie within calculated error bars of each other and yet the difference seems more systematic; the reason for the difference could not be found.

The time for the hydrogen to dissociate in the stagnation region is estimated in Appendix G to be less than 100  $\mu$ sec for conditions produced by incident shock velocities of 1.9 mm/ $\mu$ sec and higher. This is roughly the time required to start the nozzle; thus, it is felt that data obtained at this velocity and higher could be interpreted. Interpretation of the data at lower shock velocities would be complicated by the H-atom concentration varying in time and location in the stagnation region.

These data for  $U_s \ge 1.9 \text{ mm/}\mu\text{sec}$  can be interpreted either under the assumption that  $\phi = 7$  in the 100% CO is due to an unknown impurity (perhaps H-atoms) or under the assumption that  $\phi = 7$  is due to a property of the CO molecule itself. Under the first assumption a simple analysis can be applied to the 250 ppm of H<sub>2</sub> data to obtain a quantitative estimate of the efficiency of H-atoms in relaxing CO. This is done by first considering the expression for the relaxation time of CO in a mixture of CO + H-atoms + unknown impurity.

$$\frac{I}{\tau_{\text{CO-mix}}} = \frac{I - f_i - f_H}{\tau_{\text{CO-CO}}} + \frac{f_i}{\tau_{\text{CO-i}}} + \frac{f_H}{\tau_{\text{CO-H}}}$$
(IV-1)

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 $\tau_{\rm CO-mix}$  = relaxation time of CO in the mixture of CO, unknown impurity, and hydrogen atoms.

f; = mole fraction of unknown impurity.

 $f_{H}$  = mole fraction of hydrogen atoms.

$$\tau_{\text{CO-i}}$$
 = relaxation time of CO dilute in an infinite bath  
of the impurity i.

$$\tau_{\text{CO-H}}$$
 = relaxation time of CO dilute in an infinite bath  
of hydrogen atoms.

 $\tau_{CO-CO}$  = relaxation time of pure CO as given by Hooker and Millikan.<sup>12</sup>

If  $f_i$  and  $f_H$  are much less than one, they may be neglected in the first term on the right. The quantity  $f_i/\tau_{CO-i}$  may be evaluated by applying this equation to the results for 100% CO where the measurements give

$$\tau_{\rm CO-mix} \simeq \tau_{\rm CO-CO}/7$$
.

$$\frac{7}{\tau_{\text{CO-CO}}} = \frac{1}{\tau_{\text{CO-CO}}} + \left(\frac{f_{i}}{\tau_{\text{CO-i}}}\right)$$
(IV-2)

 $\mathbf{or}$ 

$$\frac{\tau_{i}}{\tau_{CO-i}} = \frac{6}{\tau_{CO-CO}}$$
(IV-3)

This equality is valid for the range of freezing temperatures of the measurements in "pure CO" ( $2000^{\circ} - 2400^{\circ}$ K). Equation (IV-1) can now be written for the mixture of CO + 500 ppm H + impurity<sup>\*</sup> for which  $\phi = 12$ . The impurity term is evaluated from (IV-3), which is justified since the 250 ppm H<sub>2</sub> results gave nozzle freezing temperatures around  $2000^{\circ}$ K.

<sup>&</sup>lt;sup>\*</sup>250 ppm H<sub>2</sub>  $\rightarrow$  500 ppm H can be seen to be true for U<sub>s</sub>  $\geq$ 1.9 mm/ $\mu$ sec from Fig. 32.

$$\frac{12}{\tau_{\rm CO-CO}} = \frac{1}{\tau_{\rm CO-CO}} + \frac{6}{\tau_{\rm CO-CO}} + \frac{5 \times 10^{-4}}{\tau_{\rm CO-H}}$$
(IV-4)

$$\frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-H}} = 1.0 \, {\rm x} \, 10^4 \quad . \tag{IV-5}$$

or

H-atoms are thus seen to be about  $10^4$  more efficient than CO in vibrationally relaxing CO. This is an anomalously high efficiency for vibrational relaxation; however, a similar high efficiency has been observed for the relaxation behind shock waves of  $O_2$  and  $N_2$  by O-atoms. In writing equation (IV-4) it was assumed that the H-atom mole fraction remained at its value in the stagnation region during the nozzle expansion. If appreciable recombination does occur the effect on the above analysis would be to raise the predicted H-atom efficiency. Analysis of the data under the assumption that  $\phi = 7$  is due to a property of the CO molecule is considered in Appendix H.

The results for 1% H<sub>2</sub> in CO have been analyzed in more detail. Stagnation conditions for this mixture were found by including H<sub>2</sub> vibration and dissociation in the equilibrium reflected shock calculations. The details of this and the nozzle flow calculations for the CO + H<sub>2</sub> + H mixtures are given in Appendix D. In the nozzle calculations the H-atom mole fraction was assumed fixed at its value in the stagnation region, so that the only free parameter was  $\tau_{\rm CO-H}$  and its variation with temperature. No allowance was made for possible impurity being responsible for  $\phi = 5$  in 100% CO since the 1% hydrogen should dominate the CO relaxation. For the calculations, an assumption was made that  $\tau_{\rm CO-H} = \tau_{\rm CO-H_2/Y}$  where Y is a free parameter and  $\tau_{\rm CO-H_2}$  is given by Hooker and Millikan. <sup>12</sup> Results from these calculations are shown with the 1% H<sub>2</sub> + 99% CO data

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in Fig. 34. It can be seen from this figure that the temperature dependence of  $\tau_{\rm CO-H}$  is not that of  $\tau_{\rm CO-H_2}$ , since the data do not lie along any single curve. The value of  $\tau_{\rm CO-H}$  for the various points can be obtained for shock velocities around 1.9 mm/µsec and higher from this figure as some fraction (1/Y) of  $\tau_{\rm CO-H_2}$  and plotted vs freezing temperature. Figure 35 shows this along with other relaxation times for comparison. The results shown indicate that H-atoms are four orders of magnitude more efficient that CO in vibrationally relaxing CO at temperatures around  $1500^{\circ}$ K. This result is similar to that obtained earlier in analyzing the 250 ppm data at 2000<sup>°</sup>K, which is also shown in this figure. It is not felt that the temperature dependence indicated by the dashed line is significant in view of the limited temperature range of the data.

As mentioned earlier, the data at shock velocities below 1.9 mm/ $\mu$ sec come from a gas whose initial conditions may be changing with time due to the continued dissociation of hydrogen in the stagnation region during an experiment. Nevertheless they can be discussed qualitatively. One does see in these data a definite correlation between decreasing  $\phi$  and decreasing equilibrium H-atom concentration as the shock velocity is lowered. However, at shock velocities around 1.5 mm/ $\mu$ sec the data are lower than any of the curves; at this velocity there is only about 100 ppm of H-atoms at equilibrium in the stagnation region, so that varying their efficiency (i.e. Y) has very little leverage on the vibrational temperatures in the nozzle. Hence, these data should be understandable simply on the basis of the equations for a CO-H<sub>2</sub> mixture and the known<sup>12</sup> relaxation times for CO and H<sub>2</sub>. The analysis described earlier reduces to this description in the absence of H-atoms so it is not known why the data fall short of the curves as they do.

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The radiation vs time in the nozzle did not change qualitatively as shock velocity was lowered until 1.53 mm/ $\mu$ sec. If the hydrogen were continuing to dissociate in the stagnation region during an experiment, one would expect to see a continuous drop in signal downstream in the nozzle since the increasing H-atom concentration would cause the relaxation time for the mixture to continually decrease. Less important effects would be a small drop in stagnation pressure and temperature due to hydrogen dissociation which would tend to lengthen the relaxation time but decrease the initial gas temperature and density, and hence signal in the nozzle. In fact, the signals to do the opposite; they start low and increase to a maximum after 300-400  $\mu$ sec and then level off or begin decreasing. In the two lowest shock velocity runs the signals were still rising 500  $\mu$ sec after nozzle start-up when the oscillogram ended. The data for which this occurred are plotted in Figs. 33 and 34 with error bars indicating the low initial signal and the maxiumum signal reached on the oscillogram.

Electrons have been mentioned to the author as an impurity which may have been responsible for the efficient relaxation of  $N_2$  and CO and consequent high values of  $\phi$  reported by those workers who have used the line reversal technique. Those experiments employing the line reversal technique would definitely experience an increase in electron concentration due to the sodium or chromium which were added as tracer elements to follow the vibrational relaxation. Since the present work used a passive measurement technique, it was decided to add chromium carbonyl to the test gas in the same manner as was done at CAL<sup>5</sup> and to look for any effect on the relaxation.

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Experiments were run in mixtures of 0.1%  $Cr(CO)_6 + CO$  (unfiltered General Dynamics C. P. grade) and no change was observed from the  $\phi = 10$  result which was being obtained at that time. Since this is roughly the same concentration of  $Cr(CO)_6$  used at CAL, it is unlikely that this seed had any direct effect on the flow or vibrational relaxation in their work.

The error bars shown on the data in Figs. 26 and 30 were calculated based on the uncertainties in the measured quantities: (1)  $P_1$ , 5% (2)  $T_1$ , 1.5% (variations in room temperature from day to day;  $T_1 = 294^{\circ}K$  was used in all calculations) (3) distance between heat transfer gauges, 2% (due to finite width of heat transfer elements) (4) time for shock passage between heat transfer gauges, 1.5% (5) signal 5% and (6) mirror area, 4%. In addition a systematic error could result from an incorrect estimate of the boundary layer thickness in the nozzle; the most direct result of this would be its effect on the density predicted in the nozzle. To a certain extent the agreement in Figs. 30 and 31 for results at area ratios 10 and 35 confirm that the boundary layer is adequately predicted since vibrational temperature is calculated to be frozen before area ratio 10, and there is only the density drop between these locations to be accounted for in interpreting the data. Measurements of nozzle pressure to stagnation pressure scattered between values predicted by the displacement thickness equal to zero and to twice the calculated value. Such an uncertainty gives a  $\pm$  7% uncertainty in the density at area ratio 10 which is roughly equivalent to a  $\pm$  70  $^{\circ}$ K vertical displacement of the data in Fig. 26. Finally, there is a remaining uncertainty in the gas purity in the experiment. This is felt to be a very important aspect of the experiments because of the large effect certain

impurities can have on the relaxation. Reasonable precautions have been taken to insure the purity of the gas and of the apparatus, and have been described in the previous sections. Yet, in view of the very high efficiency found for the hydrogen atom and its availability in various forms such as water vapor and hydrocarbons, and in view of the high efficiencies found by other workers for other atomic species, there remains some doubt as to the interpretation of the  $\phi = 5$  result found for pure CO. The mass spectrometer analysis has shown that there is no important H<sub>2</sub> concentration in the gas used; it is conceivable however that large (mass greater than 100 atomic mass units) hydrogen containing molecules could be contaminating the gas. Such a hypothesis would seem unlikely in view of the liquid nitrogen trap through which the gas is passed and yet the seeming reduction toward  $\phi = 1$  in the CO-argon results is not inconsistent with this interpretation. A more reasonable possibility would be for impurity adsorbed on the shock tube walls to be released into the gas behind the reflected shock through the mechanism of the end wall boundary layer. Doubts were cast on this explanation by the results of a series of experiments in which the gas pressure was varied; these results indicated a saturation level of pressure (at  $P_1 = 4$  cm) beyond which increasing the pressure brought no further de**c**rease in  $\phi$ .

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#### V. DISCUSSION

It is felt that a proper statement of the results described here is that  $\phi \leq 5$  for pure CO and for 5% CO + 95% Ar. These results are clearly in disagreement with earlier work in this area by Hall and Russo<sup>6</sup> and by Russo<sup>7</sup> who found  $\phi = 100$  for the Na-line reversal measurements and  $\phi = 1000$  in the infrared band reversal measurements in 5% CO + 95% They also used a shock tunnel generated expansion flow of quite argon. similar geometry and gas conditions to that described here. Their work appears to have been carefully performed and yet there is some reason for concern with how well they knew the purity of their gas mixture. Russo states that he used C. P. grade carbon monoxide with a purity level given by the manufacturer of 99.5% and Argon of 99.996% purity. Thus, the purity of his mixture should be about 99.975%. He considers that an adequate test for impurities is to measure the relaxation time behind incident shocks, and indeed he obtains the proper value in such measurements. He further argues that since any molecular impurities in the gas will be likely to dissociate behind the reflected shock and not recombine in the subsequent expansion, that such impurities would exhibit their greatest effect in the incident shock wave measurements. This argument is reasonable based on the known high efficiencies of molecular impurities in deexciting diatomic species, but it does not account for the recently found high efficiencies of atomic species. A similar argument explains why atoms are important in nozzle flow experiments and not behind shock waves. For example, the 0.2% H<sub>2</sub> + 99.8% CO which gave  $\phi = 100$  in this work would only exhibit a factor of 1.3 decrease in relaxation time in measurements

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behind incident shock waves where the  $H_2$  remains undissociated. It is likely that an even smaller concentration would be required in a 5% CO + 95% Ar mixture to produce a similar result because  $\tau_{CO-Ar} \simeq 4 \tau_{CO-CO}$  at freezing temperatures for  $\phi = 100$  in this mixture. Thus, hydrogen atoms would look even more efficient in relaxing CO when the comparison was with argon. In Appendix J it is estimated that only 0.125%  $H_2$  in 5% CO + 95% Ar would give  $\phi = 100$ . This would be a greater impurity content then Russo quotes for his gas. This level of impurity does not seem a remote possibility, however, in view of the author's difficulty in obtaining pure gas, even when buying research grade with analysis supplied.

Holbeche and Woodley<sup>8</sup> have also examined the vibrational relaxation of CO in an expansion flow; they measure  $\phi = 1$ . Their experiments were performed in a shock-expansion tube for vibrational temperatures in the stagnation region and in the expansion around 2300° to 2000°K, respectively. The results of this thesis are not in disagreement with their work since at these conditions this nozzle flow experiment cannot distinguish between  $\phi = 1$  and  $\phi = 5$ .

In view of the similarities of CO and  $N_2$ , it would seem relevant to reconsider the work which has been performed in nitrogen. Examination of Fig. 2 shows that there has been a range of results covering almost 3 orders of magnitude in the value of  $\phi$ . One fact is clearly evident in all of these works and that is that none have given a quantitative specification of their gas purity such as can be obtained from a mass spectrometer analysis. Holbeche and Woodley observed the least discrepancy between relaxation in expansion and relaxation behind shock waves, yet they

clearly state that they did not know the purity of their gas. Hurle, Russo, and Hall gave a very complete account of their apparatus and their development of the line reversal method for these measurements, but they state the impurity of their gas as being less than 100 ppm without giving the source of this figure. In a subsequent paper, Russo<sup>43</sup> addressed the impurity question directly by <u>adding</u> different impurities  $(CO_2, O_2, C_2H_2, H_2O)$  in varying amounts. He observed there was no effect on his measurements in the nozzle until their concentration was roughly 1000 ppm or larger, with the  $C_2H_2$  showing the most pronounced effect. He quoted the earlier paper in stating that his pure N<sub>2</sub> had no more than 100 ppm of impurity. Without justification of this number such results are meaningless. If the nitrogen relaxation is already controlled by another species, then adding more of it will do nothing until the added concentration is comparable to the original level.

Sebacher<sup>9</sup> measured the relaxation of nitrogen and nitrogen in air in an arc tunnel and obtained  $\phi = 15$ . Regarding his nitrogen measurements, he quotes a water vapor content of .001%, but gives no further quantitative information on his nitrogen purity. His failure to observe any effect due to adding up to 0.1% H<sub>2</sub>O to his gas cannot be interpreted as indicating that this amount of water vapor is unimportant in the relaxation of <u>pure</u> nitrogen. His measurements of the relaxation of nitrogen in air gave the same results as his measurements in nitrogen. He interprets this as indicating that the effects of O<sub>2</sub> and NO (up to 3%) are unimportant in the relaxation of nitrogen. This only indicates to the author that his relaxation is already dominated by some species other than nitrogen. His plot of transition probabilities from which he further

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justifies this result has several errors, the most serious of which is his representation of  $P_{10}$  for  $N_2$  T-V exchange; it is shown too large by three orders of magnitude.

Petrie, in an experiment similar to Sebacher's, but at higher stagnation temperatures, examined the relaxation of N<sub>2</sub> in a mixture of high temperature air consisting of almost fully dissociated oxygen, partially dissociated nitrogen and 1.6% NO, and compared his results to the relaxation times of pure N<sub>2</sub> behind shock waves and obtained  $\phi = 150$ . He does not account for the very important known effect<sup>45,46</sup> of these other species on the N<sub>2</sub> relaxation.

Recently Bray<sup>47</sup> and Treanor, Rich, and Rehm<sup>48-50</sup>, have proposed theoretical models which qualitatively explain why one should expect  $\phi > 1$  for an anharmonic oscillator in an expansion flow. The important properties of an anharmonic oscillator on which the theories are dependent are:

- The transition probabilities for exchange between translation and vibration (T-V exchange) increase exponentially with quantum number.
- (2) The probabilities for exchange of energy among the vibrational energy levels (V-V exchange) are orders of magnitude larger than the probabilities for T-V exchange for the lower quantum levels but not for the upper quantum levels.
- (3) Energy can be exchanged with translation in a V-V exchange because of the non-uniform spacing of the energy levels for an anharmonic oscillator.

Treanor<sup>48</sup> has shown by a limiting form of the master equation, for an anharmonic oscillator with single quantum V-V exchange, and by a statistical mechanic approach that in the limit of large V-V rates compared to T-V rates for all quantum levels (a distortion of property 2) one obtains a non-Boltzmann population of the energy levels. The upper levels in his solution are considerably more populated than in a Boltzmann distribution. Treanor notes that this growth of upper level population is eventually truncated by the high upper level T-V rates. Bray<sup>47</sup> and Rich and Rehm<sup>49</sup> treat the relaxation of an anharmonic oscillator with properties (1) - (3) and show that energy relaxation is favored in an expansion flow because energy is drained rapidly by high upper level T-V rates from the initially excited upper quantum levels with these levels repopulated during the relaxation by rapid V-V exchange.

There is some uncertainty in calculating  $\phi$  within the framework of these theories because they depend critically on the transition probabilities for V-V exchange and T-V exchange throughout the vibrational ladder, and detailed knowledge of these for V-V exchange is only known from theoretical calculations. Only Bray has given numerical calculations to deal with results of measurements of relaxation in various flow situations. In his work he uses transition probabilities similar to those given theoretically by Schwartz, Slawsky, and Herzfeld<sup>51, 52</sup> (SSH theory). He then varies these probabilities to see what is required to match existing data. His calculations for the expanding nitrogen flow of Hurle, Russo, and Hall<sup>5</sup> indicate that a considerable increase of upper level transition probabilities would be required to give agreement between his theory and their experiments.

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An equally important effect of the theories with regard to the interpretation of experiments is that the predicted non-Boltzmann distribution of vibrational energy precludes the definition of a vibrational temperature in the usual sense, and it becomes necessary to speak of a "temperature" for each of the various vibrational levels. In this work the measurements mainly reflect the temperature of the v = 2 level while the band reversal (fundamental band of CO) measurements of Russo mainly reflect the temperature of the v = 1 level; the sodium line reversal measurements of Holbeche and Woodley and Russo reflect the temperature of the v = 8 level. The theoretical results of Treanor, Rich, and Rehm for the case of large V-V rates compared to T-V rates indicate that there should only be about 1% difference in temperature of the v = 1 and v = 2 levels and about 5% difference in temperature of the v = 1 and v = 8levels, for the freezing temperatures of the CO-Ar results obtained by Russo and in this work. This is a small effect in terms of the difference in results between this work and Russo's; however, it does predict about half of the difference between his line reversal ( $\phi = 100$ ) and his band reversal ( $\phi = 1000$ ) measurements.

Since the results of this work indicate that  $\phi$  may be as large as 5, it is important to consider whether the results could be explained on the basis of the theories mentioned. In the absence of quantitative predictions by the theories, one can only speculate. Drs. Bray and Treanor have indicated to the author that they do feel  $\phi = 5$  can be predicted by their theories without unreasonable assumptions regarding the transition probabilities. In view of this, it remains uncertain whether the measurements given in this paper are due to the models they suggest or to residual

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impurities. Treanor, Rich, and Rehm, <sup>50</sup> and Russo, <sup>7</sup> have noted that one way to show the validity of the theories would be to investigate a mixture of a diatomic molecule very dilute in an inert gas such as Argon. If the dilution were large enough, one could expect the T-V exchange to exceed the V-V exchange, dominate the relaxation, and thereby give  $\phi = 1$ results in a nozzle flow. Such an experiment has been considered for the apparatus described here. It is estimated that the highest dilution that could be obtained and still have a useable signal to noise ratio, is 0.1% CO in Argon; this would be effected by monitoring the emission from the fundamental band. Further, it is estimated that such a dilution would just give comparable V-V and T-V rates; this estimate is based on comparing  $P_{10}$  for CO and V-V transition probabilities as given by SSH theory. Since T-V transition probabilities for the lower levels are proportional to the quantum number of the upper state, this would indicate T-V would dominate V-V exchange by an order of magnitude for v = 10and larger. Thus such an experiment does seem feasible.

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#### VI. SUMMARY

In this thesis the vibrational relaxation of carbon monoxide has been studied in the nozzle expansion of a shock tunnel by using a passive measurement technique, namely the first overtone emission of CO, to measure vibrational temperatures in the nozzle. The principal results of the measurements are that  $\phi \leq 5$  in CO and in 5% CO + Ar, where  $\phi$ is the ratio of the vibrational relaxation time of the gas behind incident shock waves to the relaxation time in the nozzle flow. This result is considerably different from that obtained ( $\phi = 100$  to 1000) by other workers measuring in a similar shock tunnel. Particular care has been taken to examine the level of impurities in the experiments and to assess their importance. In this investigation of impurities it was found that hydrogen atoms are about four orders of magnitude more efficient in vibrationally relaxing CO than CO is itself for temperatures around 1500°-2000°K; this implies they have a probability for de-excitation of CO around  $10^{-2}$ to  $10^{-1}$ . This result is similar to that obtained by other workers for the effect of O-atoms vibrationally relaxing  $N_2$  and  $O_2$  behind shock waves. These results collectively indicate the need in nozzle flow experiments for considerable care in determining the purity of the gas and in considering what species will be formed in the stagnation region by the components of the gas. Once the relaxation in a nozzle flow is well understood the shock tunnel will represent a fine device for studying the effects of atoms or radicals which can be produced in the stagnation region by chemistry or dissociation.

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#### APPENDIX A

#### OPACITY OF THE GAS

The opacity of the first overtone band of CO is considered here for the three regimes in which measurements were taken: (1) at equilibrium behind incident shock waves, (2) at equilibrium behind reflected shock waves, (3) downstream in the nozzle where a quasi-equilibrium exists. The works of Plass<sup>53</sup> and Young<sup>54</sup> are applied to these regimes to show that in each case the gas satisfied the conditions for the non-overlapping line approximation and the emissivity at the center of the strongest line in the band is small enough that the band is optically thin (radiation from it scales linearly with optical path length and the number density of CO molecules).

The term Lorentz (or Doppler) broadened line in the notation below means a line for which the Lorentz (or Doppler) broadening mechanism is the dominant one. If both mechanisms are comparable then the line is broadened more than it would be by either one acting alone.

Evaluation is greatly simplified by the results of Young's report. Following his work and notation, the absorption coefficient at the center of a Lorentz broadened line is

$$A(v_0) = 1 - e^{-2x}L$$
, (A-1)

where

A = absorption coefficient

 $v_o$  = wave number at the center of a line cm<sup>-1</sup>  $x_L$  = parameter measuring the opacity at the center of a Lorentz line,

and

$$x_{L} = \frac{Sn\ell}{2\pi\gamma_{L}}$$
(A-2)

ama<sup>-1</sup>cm<sup>-2\*</sup> = integrated line absorption coefficient S n = number density of radiating species ama  $\ell$  = path length, 3.38 cm in all cases  $\mathbf{cm}$ cm<sup>-1</sup>  $\gamma_{\rm L}$  = half width at half height of a Lorentz broadened line.

Lorentz line width is proportional to total number density

$$\gamma_{\rm L} = \gamma_{\rm o} n_{\rm t} \tag{A-3}$$

cm<sup>-1</sup>ama<sup>-1</sup>  $\gamma_{o}$  = Lorentz half width at 1 amagat; for CO,  $\gamma_0 = 0.05 \text{ at } 273.2^{\circ} \text{K}$ ama

 $n_{+}$  = total number density.

Equations (A-2) and (A-3) give

$$x_{L} = \left(\frac{S}{2\pi\gamma_{0}}\right) f \ell \qquad (A-4)$$

f = mole fraction of radiating species 
$$(=n/n_{+})$$

If  $x_{I_{i}}$  is small as in the case of an optically thin Lorentz line then expansion of (A-1) gives

$$A(v_0) = 2 x_1 + \dots$$
 (A-5)

For a Doppler broadened line the absorption coefficient at a line center is

$$A(v_0) = 1 - e^{-x_D}$$
, (A-6)

\*  $1 \text{ ama} = 1 \text{ amagat} = 2.69 \times 10^{19} \text{ particles/cm}^3$ , number density of a gas at standard conditions.

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where

$$x_{\rm D} = \left(\frac{{\rm mc}^2}{2\pi {\rm kT}}\right)^{1/2} \frac{{\rm S}}{\nu} {\rm n} t$$
 (A-7)

m	Ξ	mass of CO molecule	gm
k	=	Boltzmann's constant	erg/ <sup>0</sup> K
т	=	translational temperature	°K
ν	=	wave number of radiation	$\mathrm{cm}^{-1}$
с	=	speed of light.	cm/sec

If we not, that  $\gamma_o$  is proportional to  $\sqrt{T}$  and introduce

$$\gamma_{o} = \gamma_{oo} \sqrt{T/T_{o}}$$
 (A-8)

 $\gamma_{oo}$  = Lorentz half width at 1 ama and cm<sup>-1</sup> ama<sup>-1</sup> 273.2°K = 0.05 cm<sup>-1</sup>

$$T_{a}$$
 = standard temperature = 273.2°K

then equation (A-7) may be rewritten as

$$x_{\rm D} = \left(\frac{2\pi\,{\rm mc}^2}{{\rm k}\,{\rm T}_{\rm o}}\right)^{1/2} \frac{\gamma_{\rm oo}}{\nu} \left(\frac{{\rm S}}{2\pi\,{\rm \gamma}_{\rm o}}\right) {\rm n}\,\ell \qquad (A-9)$$
$$= 2.639\,{\rm x}\,10^6 \frac{\gamma_{\rm oo}}{\nu} \left(\frac{{\rm S}}{2\pi\,{\rm \gamma}_{\rm o}}\right) {\rm n}\,\ell \,.$$

If  $x_D$  is small as in the case of an optically thin Doppler line then expansion of (A-6) gives

$$A(v_0) = x_0 + \dots$$
 (A-10)

Thus for the gas conditions and geometry of this work  $x_L$  and  $x_D$  must be calculated and at least one of them be shown to be small. In both cases the temperature dependence of the parameter is contained in the factor  $(\frac{S}{2\pi\gamma_0})$ . Young plots this parameter vs wave number for curves of constant temperature for the first overtone and other bands. From such a plot it is easy

to recognize, for a given temperature, the maximum value of the parameter and calculate  $x_L$  and  $x_D$  for that value. When the entire band is considered in this fashion the highest values of  $(\frac{S}{2\pi\gamma_0})$  occur at the lowest temperatures. The total band radiation decreases with temperature but the radiation is carried by fewer lines of smaller half width, and the latter two effects evidently dominate. For the three regimes considered here there can be a competing trend with temperature if the lines are Doppler broadened because  $x_D \sim n$  and in this work the highest gas densities are found with the highest temperatures since gas conditions are generated by shock waves of different strengths propagating into gas of constant initial pressure. This does not turn out to be important, however, as Lorentz broadening is found to dominate or be comparable to Doppler broadening in all three cases.

Before giving the values of  $x_L$  and  $x_D$  at the lowest temperature used in each of the three regimes it is necessary to ask how small must  $x_L$  or  $x_D$ (whichever is smallest) be in order to neglect self absorption by the gas. To answer this it is necessary to calculate one additional parameter at the wave number of maximum  $(\frac{S}{2\pi\gamma_0})$ . This parameter ( $\beta$ ) measures the ratio of line width to line spacing.

$$\beta = \left(\frac{2\pi \gamma_0}{d}\right) n_t \qquad (A-11)$$

where d = line spacing.

Young also gives figures showing  $\beta$  vs wave number for lines of constant temperature. With values of  $x^*$  and  $\beta$  one can then refer to Plass and find which of his three approximations is relevant for the gas at the conditions

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The value of x may be safely taken as the smaller of  $x_L$  and  $x_D$ ; if they are comparable then it depends on both but is smaller than either one.

of interest. In all three cases below the gas was found to be described by the "non-overlapping line approximation" for either a statistical or an Elsasser band model (Plass Figs. 2 and 4); thus it could be seen that for  $x \leq 0.3$  (Plass Fig. 8) the absorption coefficient for a band should be

$$A = \beta x = \frac{S n \ell}{d} , \qquad (A-12)$$

and the gas should be optically thin. If  $x \leq 0$ , 1 at line centers one would not worry about the effects of self-absorption; however in some cases x was larger and this additional examination shows that when such lines are taken together to form a band the fact that some of the radiation comes through the wings of the line helps to raise the upper limit of x at which the band can be considered thin.

Case (1): Incident shock - The worst case for the range of conditions covered was found at the lowest temperature and is presented here.

At 
$$U_s = 1.62 \frac{mm}{\mu sec}$$
  $T_2 = 1400^{\circ} K$   
 $P_2 = 0.33 \text{ atm.}$   
 $n_2 = 0.07 \text{ amagat}$ 

For these conditions,

$$\left(\frac{S}{2\pi \gamma_0}\right)_{max.} = 0.04 \text{ cm}^{-1}$$

from which

 $x_{L} = 0.14 < 0.3$ , whereas  $x_{D} = 0.3$ .

Since  $x_L$  and  $x_D$  are comparable the composite x is dependent on both, but smaller than either  $x_L$  and  $x_D$ . Since already  $x_L < 0.3$  it is not necessary to compute x. The parameter measuring line width to line spacing is

 $\beta = 0.007$ , so the lines are non-overlapping (from Plass Fig. 2 or 4). Case (2): Reflected shock

At 
$$U_s = 1.17 \frac{mm}{\mu sec}$$
  $T_4 = 1500^{\circ} K$   
 $P_4 = 3.6 atm.$   
 $n_4 = 0.7 amagat$   
 $\left(\frac{S}{2\pi \gamma_o}\right)_{max.} = 0.04 \text{ cm}^{-1}$   
 $x_L = 0.14 < 0.3$ , whereas  $x_D = 3.0$  so the  
line is basically Lorentz broadened  
 $\beta = 0.07$ , and the gas is described by the non-  
overlapping line approximation.  
Case (3): Nozzle flow - Here we must recognize the quasi-equilibriu

Nozzle flow - Here we must recognize the quasi-equilibrium nature of the gas and note that line intensity is determined by T<sub>v</sub> while line width is determined by T. The worst case was found at the lowest temperatures and is presented here.

$$\begin{split} \underbrace{\text{Stag}}_{\text{S}} & \underbrace{\text{Nozzle (Area Ratio 10)}}_{\text{T}_{\text{V}}} = 1.4 \text{ mm}/\mu \text{sec} & \text{T}_{4} = 2000^{\circ}\text{K} & \text{T}_{\text{V}} = 1900^{\circ}\text{K} \\ & \text{P}_{4} = 6 \text{ atm.} & \text{T} = 500^{\circ}\text{K} \\ & \text{n}_{4} = 0.9 \text{ amagat} & \text{n} = 0.03 \text{ amagat} \\ & \left\{ \frac{\text{S}}{2\pi \gamma_{0}} \right\}_{1900^{\circ}\text{K}} = 3 \cdot 10^{-2} \text{ cm}^{-1} , \gamma_{0} \sim \sqrt{\text{T}} \\ & \frac{\text{S}(1900^{\circ}\text{K})}{2\pi \gamma_{0}(500^{\circ}\text{K})} = 3 \times 10^{-2} \cdot \sqrt{\frac{1900}{500}} \sim 6 \cdot 10^{-2} \text{ cm}^{-1} \\ & \text{x}_{\text{L}} = 0.2, \text{ and } \text{x}_{\text{D}} = 0.17 < 0.3 . \\ & \beta = 0.003 . \end{split}$$

Thus it is seen in all three cases that  $x \le .3$ , so that equation (A-12) is valid, and radiation is proportional to number density of radiating species and path length.

#### APPENDIX B

### END WALL BOUNDARY LAYER

When the incident shock is reflected, hot stagnation region gas is suddenly placed in contact with the cold (room temperature) end wall. An estimate is desired of the effect of the cooling of the stagnation region gas, by the end wall thermal boundary layer, on the condition of the gas which flows down the nozzle. In the calculations below, the heat loss through this boundary is compared to the thermal energy of the gas flowing out the nozzle. First, however, a rough estimate of the boundary layer thickness is given. This is done by considering the incompressible problem, which is the classical Stokes <sup>55</sup> problem.

If the edge of the boundary layer is arbitrarily defined as that point where

$$\frac{T_{\infty} - T}{T_{\infty} - T_{w}} = .01$$
 (B-1)

then the boundary layer thickness is given<sup>55</sup> by

$$\delta = 4 \sqrt{at} . \tag{B-2}$$

$$T_{\infty}$$
 = temperature outside the boundary layer in  
the stagnation region = 3000<sup>°</sup>K for these  
calculations.

T = temperature at any point in the boundary layer.

$$T_{\rm m}$$
 = wall temperature = 300<sup>°</sup>K

$$\delta$$
 = boundary layer thickness cm  
 $a$  = thermal diffusivity =  $\frac{k}{\rho C_p}$  cm<sup>2</sup>/sec

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k = thermal conductivity  $erg/sec-cm^{\circ}K$   $\rho$  = gas density  $gm/cm^{3}$  $C_{p}$  = specific heat at constant pressure  $erg/gm^{\circ}K$ 

For upper and lower bounds on  $\delta$  use

$$a_{\infty} \simeq .6 \frac{\text{cm}^2}{\text{sec}}$$
 at  $3000^{\circ}$ K  
 $a_{w} \simeq .018 \frac{\text{cm}}{\text{sec}}$  at  $300^{\circ}$ K

so that for t = 500  $\mu$ sec (the maximum duration of a test)

## $0.012 \text{ cm} < \delta < 0.07 \text{ cm}$

For the <u>compressible</u> end wall thermal boundary layer Kemp<sup>59</sup> gives a solution for the heat flux at the wall based on a similarity solution to the problem. For the heat flux he finds

$$\dot{q}_{w} = \left\{ \begin{array}{c} \frac{k}{C_{p}} & \frac{\partial h}{\partial y} \\ \end{array} \right\}_{w} = \left\{ \begin{array}{c} \frac{\rho_{\infty} k_{\infty}}{2 C_{p_{\infty}} t} \\ \end{array} \right\}^{1/2} h_{\infty} G_{w}$$
(B-3)

where

$$G = K g_{\eta}$$
 (B-4)

$$K = (\rho k/C_p) / (\rho k C_p)_{\infty}$$
(B-5)

$$g_{\eta} = \frac{\partial g}{\partial \eta}$$
(B-6)

$$g(\eta) = h/h_{\infty}$$
(B-7)  

$$\eta = \text{similarity variable} = \begin{cases} C_{p \infty} \\ \frac{1}{2t\rho_{\infty}k_{\infty}} \end{cases} \int_{0}^{1/2} \int_{0}^{y} \rho \, dy$$
(B-7)  

$$h = \text{enthalpy} , \text{erg/gm}$$
  

$$t = \text{time} , \text{sec}$$
  

$$\dot{q}_{w} = \text{heat flux at the wall, erg/sec-cm}^{2}$$

He finds upper and lower bounds for  $\boldsymbol{G}_{\boldsymbol{\mathrm{W}}}$  as

$$G_{w_o} < G_w < \sqrt{2} G_{w_o}$$
 (B-8)

where

$$G_{w_0}^2 = \int_{g_w}^{1} (1 - g) K dg$$
 (B-9)

For a power law variation of K =  $g^{\omega-1}$ , he evaluates (B-9) to obtain

$$G_{w_{o}} = \left\{ \frac{1 - g^{\omega}_{w}}{\omega} - \frac{1 - g^{\omega+1}_{w}}{\omega+1} \right\}^{1/2}$$
(B-10)

Equations (B-3) with (B-8) and (B-10) can be used to obtain an upper bound for  $\dot{q}_w$ . Assuming  $\omega = 1/2$  (i.e.  $K = g^{-1/2}$  or  $k \sim \sqrt{T}$ ,  $\rho \sim T^{-1}$ , and  $C_p = \text{const.}$ ), the stagnation conditions of  $P_{\infty} = 10$  atm,  $T_{\infty} = 3000^{\circ}$ K and the other gas properties listed below, the calculation is straightforward.

$$\rho_{\infty} = 1.25 \cdot 10^{3} \text{ gm/cm}^{3}$$

$$k_{\infty} = 8. \cdot 10^{3} \text{ erg/sec-cm-}^{\circ} \text{K}$$

$$C_{p_{\infty}} = 1. \cdot 10^{7} \text{ erg/gm-}^{\circ} \text{K}$$

$$h_{\infty} = C_{p_{\infty}} T_{\infty}$$

$$g_{w} = 0.1$$

$$G_{w} = 0.855$$

$$\dot{q}_{w} = 2.52 \cdot 10^{7} \text{ t}^{-1/2}$$

For a 500 
$$\mu$$
sec period,  $5 \cdot 10^{-4}$   
 $q_w = A_w \int_{0}^{10} \dot{q}_w dt = 1.29 \cdot 10^7 erg$  (B-11)

 $A_{w}$  = area of shock tube end wall = 11.4 cm<sup>2</sup>

The thermal energy of the gas which flows out the nozzle in this period is

$$Q = \dot{m}h_{m}t \qquad (B-12)$$

where

$$m = mass flow rate$$
,  $gm/sec$   
 $\dot{m} = (\rho A u)_{throat}$  (B-13)

using 
$$\gamma = 1.4$$
 isentropic flow relations,  
 $\rho_t \simeq 0.634 \rho_{\infty}$   
 $A_t = 0.428 \text{ cm}^2$   
 $u_t = \text{speed of sound at throat} \simeq 9.9 \cdot 10^4 \text{ cm/sec}$   
so  $\dot{m} = 33.7 \text{ gm/sec}$   
and  $Q = 5.05 \cdot 10^8 \text{ erg}$  (B-14)

$$\frac{q_{\rm w}}{Q} = 0.0255$$
 (B-15)

Thus, even if <u>all</u> of the heat lost from the stagnation region is taken from that gas which flows down the nozzle, there is only a 2.5% energy loss from that gas.

#### APPENDIX C

### NOZZLE BOUNDARY LAYER

The boundary layer displacement thickness at the nozzle throat was estimated with the results of Cohen and Reshotko<sup>34</sup>, who considered the similarity solution of compressible laminar boundary layers with heat transfer and pressure gradient. An outline of the solution is given here using their notation.

$\mathbf{T}_{\mathbf{w}}$	=	300 <sup>0</sup> К	<b>,</b>	wall temperature
$^{\mathrm{T}}{_{\infty}}$	=	3000 <sup>0</sup> К	3	stagnation temperature
s <sub>w</sub>	=	$\frac{h}{w}{h_{\infty}} = 1$	,	enthalpy parameter

so

$$S_w \simeq -.9$$

The pressure gradient parameter  $\beta$  was set equal to zero (flat plate value); this gives an upper bound to the displacement thickness since a favorable pressure gradient actually exists.

Then Table II of their paper is interpolated to obtain

$$\frac{\delta^*}{X} \left\{ \frac{m+1}{2} \quad \frac{U_e X}{v_o} \right\} \simeq 0.1218$$

where for this problem

 $U_{e} = 8.8 \cdot 10^{4} \text{ cm/sec}, \text{ throat velocity}$   $\nu_{o} = 0.45 \text{ cm}^{2}/\text{sec}, \text{ kinematic viscosity}$   $m = 0, \text{ since } \beta = 0$   $\int_{a}^{x} P_{e} a_{e}$ 

$$X = \int_{0}^{\infty} \lambda \frac{P_{e}}{P_{o}} \frac{a_{e}}{a_{o}} dx \leq \lambda x$$

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$$\lambda \simeq 2.4$$
 , viscosity parameter  
 $x \simeq 0.4$  cm , flow length from stagnation region to  
the throat  
Subscript: e - edge of boundary layer  
o - stagnation value

By using  $X = \lambda x$  an upper bound to the displacement thickness is obtained as

or  $\frac{\delta^*}{t} \sim 0.6\%$  at the nozzle throat,

where t = 0.125 cm, throat height

Thus the displacement thickness at the throat is of negligible importance.

#### APPENDIX D

## CALCULATIONS FOR H2-CO MIXTURES

## (1) Shock Calculations

The stagnation conditions for the nozzle flow are calculated from a frozen-incident/equilibrium-reflected shock model. First we write the enthalpy for a 3-component gas mixture consisting of CO, H<sub>2</sub>, and H.

R<sub>i</sub> = universal gas constant/molecular weight of

species i  $erg gm-species i-^{OK}$ 

q<sub>i</sub> = gms of species i/gm of mixture

 $\sigma_i$  = vibrational energy of species i, erg/gm-species i

 $D = dissociation energy of hydrogen \frac{erg}{gm-hydrogen}$ 

 $\theta_i$  = characteristic vibrational temperature of species i,  ${}^{o}K$ 

$$\overline{\sigma_i} = \frac{\frac{R_i \theta_i}{\theta_i}}{\frac{\theta_i / T_i}{e^{\theta_i} - 1}}$$
(D-2)

The solution for the frozen-incident shock is trivial since the last three terms in the enthalpy due to vibrational energy and dissociation of the hydrogen are neglected and  $q_{H_2} = \overset{o}{q}_{H_2}$  is specified while  $q_H = 0$  and  $q_{CO} = 1 - \overset{o}{q}_{H_2}$ . It is merely necessary to find the ratio of specific heats

<sup>\*</sup> Molecular constants were obtained from Herzberg<sup>56</sup> and NBS<sup>57</sup> circular 467.

for a CO-H<sub>2</sub> mixture and apply the Rankine-Hugoniot relations.

$$\gamma = \frac{C_p}{C_v}$$
(D-3)

$$C_{p} = \frac{7}{2} R_{mix}$$
,  $C_{v} = \frac{5}{2} R_{mix}$  (D-4,5)

$$R_{mix} = R_{CO} q_{CO} + R_{H_2} q_{H_2} + R_{H} q_{H}$$
 (D-6)

For the equilibrium reflected shock solution we must write the 3 conservation relations for mass, momentum, and energy across the shock in coordinates fixed to the reflected shock

$$\rho_2(u_4 - v_2) = \rho_4 u_4 \tag{D-7}$$

$$p_2 + \rho_2 (u_4 - v_2)^2 = p_4 + \rho_4 u_4^2$$
 (D-8)

$$h_2 + \frac{1}{2} (u_4 - v_2)^2 = h_4 + \frac{1}{2} u_4^2$$
 (D-9)

Subscripts 2 and 4 refer to conditions behind the incident and reflected shock respectively (see Fig. 4); all subscripted 2 variables are known from the frozen-incident shock solution.

 $u_4 = velocity$  with which the reflected shock propagates away from the end wall (positive number), cm/sec  $v_2 = velocity$  of the gas behind the frozen-incident shock away from the end wall (negative number), cm/sec  $(u_4 - v_2) = |u_4| + |v_2|$ , velocity of gas coming into the reflected shock in coordinates fixed to the reflected shock.

The enthalpy  $h_4$  contains all of the terms given in equation (D-1). To complete the set of equations we need the law of mass action to determine  $q_H$  behind the reflected shock.

$$\frac{a^{2}}{1-a} = \frac{m_{H}^{3/2} v_{H_{2}}}{16\pi^{1/2} I_{H_{2}}(kT)^{1/2}} \frac{g_{0}^{2}}{g_{0}_{H_{2}}} \frac{e^{-D'/T}}{g_{0}_{H_{2}}} \quad (D-10)$$

$$D' = \text{dissociation energy of } H_{2}, D' = \frac{2D}{kA_{n}}, {}^{0}K$$

$$a = \text{degree of dissociation} \frac{n_{H}}{2 n_{H_{2}}}$$

$$n_{H_{2}} = n_{H_{2}} + \frac{1}{2} n_{H} \qquad \text{cm}^{-3}$$

$$m_{H} = \text{mass of hydrogen atom} \qquad \text{gm}$$

$$v_{H_{2}} = \text{vibrational frequency of } H_{2} \qquad \text{sec}^{-1}$$

$$I_{H_{2}} = \text{rotational moment of inertia of } H_{2} \qquad \text{gm-cm}^{2}$$

$$g_{0} = \text{ground state degeneracy of species i}$$

$$A_{n}^{1} = \text{Avagadro's number} \qquad \text{for the ribustion particles/mole}$$

This form assumes  $kT/h_{\nu}$  for the vibration partition function (i.e. fully excited vibration). The following relations are also required.

$$q_{H} = a q_{H_{2}}, q_{H} + q_{H_{2}} = q_{H_{2}}^{o}$$
 (D-11, 12)

$$q_{CO} = 1 - q_{H_2} - q_{H}$$
,  $p = \rho R_{mix} T$  (D-13, 14)

$$R_{mix} = q_{CO} R_{CO} + q_{H_2} R_{H_2} + q_{H} R_{H}$$
 (D-15)

The transcendental set of 9 equations D-1, 7-14 with  $\sigma$  defined by (D-2) are then solved together for  $p_4$ ,  $\rho_4$ ,  $T_4$ ,  $h_4$ ,  $u_4$ , a,  $q_H$ ,  $q_{H_2}$ , and  $q_{CO}$ ; solution is by Newton iteration on a computer.

#### (2) Nozzle Flow

A solution based on the method of Stollery and Smith<sup>37</sup> was used. The gas composition is assumed fixed as that calculated above for the stagnation

region so that  $q_{H}$ ,  $q_{H_2}$ , and  $q_{CO}$  are constant. The "equilibrium" solution with this fixed composition is then determined by equations D-1, 2, 16-19.

$$\rho Au = M$$
 (D-16)  
h +  $\frac{u^2}{2} = H$  (D-17)

$$\frac{5}{2} R_{\text{mix}} \ln T - R_{\text{mix}} \ln p + q_{\text{CO}} R_{\text{CO}} \left[ -\ln(1 - e^{-\theta} CO/T) \right] + \frac{\theta CO/T}{e^{\theta} CO/T} + \ln \frac{T}{\theta} + 1 + q_{\text{H}_2} R_{\text{H}_2} \left[ -\ln(1 - e^{-\theta} H_2/T) \right]$$

$$+ \frac{\theta_{H_2/T}}{\theta_{H_2/T}} + \ell n - \frac{T}{2\theta_{R-H_2}} + 1] = S_0$$
 (D-18)  
e -1

$$p = \rho R_{mix} T D-19)$$

The constants H and  $S_0$  are evaluated in the stagnation region. The mass flow is determined from the condition that the velocity equals the equilibrium speed of sound at the throat.

at A/A<sup>\*</sup>, 
$$u = \left\{ \frac{\partial h/\partial T}{\partial h/\partial T - R_{mix}} R_{mix} T \right\}^{1/2}$$
 (D-20)

The variation of p and T in the nozzle is determined from this equilibrium solution and used to specify the variation of  $\overline{\sigma}$  (T) and  $\tau$  (p, T,  $\phi$ ); with this the Bethe-Teller equation for the vibrational relaxation of CO is integrated from the stagnation region down the nozzle.

$$\frac{d\sigma}{dx} = \frac{\sigma - \sigma}{u \tau_{e}}$$
(D-21)

$$\tau_{\rm e} = \tau_{\rm s} / \phi \, {\rm P(atm)}$$
 (D-22)

$$\frac{1}{\tau_{\rm s}} = \frac{f_{\rm CO}}{\tau_{\rm CO-CO}} + \frac{\tau_{\rm H_2}}{\tau_{\rm CO-H_2}} + \frac{f_{\rm H}}{\tau_{\rm CO-H}}$$
(D-23)

with each  $\tau$  in (D-23) evaluated at 1 atm.

The number density fractions are related to the mass density fractions by

$$n_{i} = \frac{\rho q_{i}}{m_{i}}$$
(D-24)

$$f_{i} = \frac{n_{i}}{\sum_{i=1}^{D} n_{i}}$$
(D-25)

the relaxation times  $\tau_{\rm CO-CO}$  and  $\tau_{\rm CO-H_2}$  are given by Hooker and Millikan<sup>12</sup> while in equation (D-23), the relaxation time  $\tau_{\rm CO-H}$  is unknown and is the free parameter in matching this solution to the H<sub>2</sub>-CO data.

Other gas dynamic properties are then obtained by the "corrected" equilibrium solution determined by equations (D-16) to (D-19) with  $\overline{\sigma}$  replaced by  $\sigma$  and  $S_{\sigma}$  replaced by S

$$\sigma = \overline{\sigma_0} + \int_0^\infty \frac{d\sigma}{dx} dx \qquad (D-26)$$

$$S = S_0 + \int_0^x \frac{d\sigma}{dx} (\frac{1}{T_v} - \frac{1}{T}) dx$$
 (D-27)

#### APPENDIX E

#### IMPURITIES OF FIXED CONCENTRATION

If one assumes that  $\phi = 5$  in pure CO at  $P_1 = 4$  cm Hg is due to an impurity whose concentration is independent of  $P_1$  then estimates of  $\phi$  at different values of  $P_1$  can be calculated.

The relaxation time for CO in a mixture with another species "i" is given by

$$\frac{1}{\tau_{\text{mix}}} = \frac{f_i}{\tau_{\text{CO-i}}} + \frac{1 - f_i}{\tau_{\text{CO-CO}}}$$
(E-1)

where

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 $\tau_{mix}$  = the relaxation time of CO in the mixture  $\tau_{CO-i}$  = the relaxation time of CO dilute in an infinite bath  $\tau_{CO-CO}$  = the relaxation time of pure CO

f. = number density fraction of species i in the mixture with each  $\tau$  in (E-1) evaluated at 1 atm. Neither f. nor  $\tau_{\rm CO-i}$  are known; however from the result of  $\phi = 5$ in pure CO at P<sub>1</sub> = 4 cm we can obtain the ratio  $f_i/\tau_{\rm CO-i}$  from equation (E-1).  $\tau_{\rm CO-CO}$  is known<sup>12</sup> at the freezing temperature,  $(1-f_i) \sim 1$  if species i is assumed to be a trace impurity, and  $\tau_{\rm mix}$  is just  $\tau_{\rm CO-CO}/5$  at the freezing temperature. Thus  $f_i/\tau_{\rm CO-i}$  is calculated at the freezing temperature  $(1900^{\circ} - 2500^{\circ} K)$ .

If one now doubles  $P_1$  to 8 cm Hg the quantity  $(\frac{f_i}{\tau_{CO-i}})$  is reduced by a factor of two under the assumption that the number density of the impurity remains constant. Therefore for the new experiment at  $P_1 = 8 \text{ cm } \tau_{\text{mix}}$  is

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calculated from equation (E-1) assuming that the freezing temperature will not change appreciably. Then  $\phi = \tau_{CO-CO}/\tau_{mix}$  and the assumption about the freezing temperature can be checked from nozzle flow calculations at this P<sub>1</sub> and  $\phi$ . For the conditions considered here, doubling the pressure tends to lower the freezing temperature while the decrease in importance of the impurity tends to raise it. The net result is that the freezing temperature only drops about 100°K, and thus will not depart appreciably from the 1900°-2500°K range.

#### APPENDIX F

## IMPURITY IN THE CO/Ar MIXTURES

The analysis here is similar to that of Appendix E. It is supposed here that the value of  $\phi = 5$  measured in "pure" CO is due to an impurity in the CO which is not present in the argon used in this work. First the ratio of the fraction of this species in the "pure" CO ( $f_i$ ) to the relaxation time of CO in an infinite bath of this species ( $\tau_{CO-i}$ ) is calculated at the freezing temperature (~2000<sup>°</sup>K) of the 100% CO experiments from equation (F-1)!

$$(\frac{f_i}{\tau_{CO-i}}) = \frac{1}{\tau_{mix}} - \frac{1}{\tau_{CO-CO}} = \frac{\phi}{\tau_{CO-CO}} - \frac{1}{\tau_{CO-CO}} = \frac{4}{\tau_{CO-CO}}$$
 (F-1)

With this we can calculate the  $\phi'$  that should be measured in a mixture of 5% CO in argon. The relaxation time of this mixture for <u>no</u> impurity in the CO is calculated by:

$$\frac{1}{\tau'_{\rm mix}} = \frac{0.95}{\tau_{\rm CO-Ar}} + \frac{0.05}{\tau_{\rm CO-CO}} \quad . \tag{F-2}$$

In the experiment the effect of the impurity mentioned is to modify this, and we measure for the mixture a relaxation time of  $\tau'_{mix}/\phi'$  where  $\phi'$  is to be estimated here by:

$$\frac{\phi'}{\tau'_{\text{mix}}} = 0.05 \ \left(\frac{f_{i}}{\tau_{\text{CO-i}}}\right) + \frac{0.95}{\tau_{\text{CO-Ar}}} + \frac{0.05}{\tau_{\text{CO-CO}}} \ . \tag{F-3}$$

The coefficient 0.05 of  $(\frac{f_i}{\tau_{CO-i}})$  is due to the assumption that the impurity is in the CO and hence is diluted along with the CO. Equation (F-3) is valid at the freezing temperature of the CO-argon experiments (~3400°K).

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Equations (F-1) and (F-2) are substituted into (F-3). The substitution of (F-1) into (F-3) requires an additional assumption that  $\tau_{\rm CO-i}$  scales with temperature in exactly the same way as does  $\tau_{\rm CO-CO}$ .

$$\phi' \left( \frac{0.95}{\tau_{\text{CO-Ar}}} + \frac{0.05}{\tau_{\text{CO-CO}}} \right) = 0.05 \left( \frac{4}{\tau_{\text{CO-CO}}} \right) + \frac{0.95}{\tau_{\text{CO-Ar}}} + \frac{0.05}{\tau_{\text{CO-CO}}}$$
(F-4)

With  $\tau_{\rm CO-Ar} = 2.5 \tau_{\rm CO-CO}$  at 3400°K equation (F-4) gives  $\phi' = 1.47$ .

#### APPENDIX G

#### HYDROGEN DISSOCIATION

The time to dissociate small amounts of molecular hydrogen present in the CO test gas is estimated here for conditions behind the reflected shock. The rate given by Jacobs, Giedt, and Cohen<sup>58</sup> for the dissociation of  $H_2$  by argon is applied to the dissociation of  $H_2$  by CO. The rate equation (G-1) is extrapolated from its value at time zero to obtain the time required for full dissociation at this initial rate.

$$\frac{d[H]}{dt} = 2k_d [H_2] [CO] - 2k_r [H]^2 [CO], \frac{moles}{cm^3 - sec}$$
(G-1)

=  $2 k_d [H_2] [CO]$ , at time = 0

$$let a \equiv \frac{[H]}{2[H_2]_0}$$
 (G-2)

where  $[H_2]_0 = \frac{\text{moles}}{\text{cm}^3}$  of  $H_2$  at time = 0

then 
$$\frac{da}{dt} = k_d [CO] \frac{[H_2]}{[H_2]_0} = k_d [CO]$$
, at time = 0 (G-3)

where  $k_d = K(T) k_r$ ,  $k_r = 10^{18} T^{-1}$  for  $H_2$  dissociated by argon<sup>58</sup>, and K(T) is the equilibrium constant, given by

$$\frac{[H]^2}{[H_2]} \equiv K(T) = \frac{m_H^{3/2} \nu (kT)^{1/2}}{4 \pi^{1/2} I_{H_2}} \frac{g_{o_H}^2}{g_{o_{H_2}}} \frac{e^{-D'/T}}{kT A_n}$$
(G-4)  
= 0.5 + 10<sup>3</sup> T<sup>-1/2</sup> e<sup>-52000°K/T</sup>

The nomenclature in equation (G-4) is the same as that used in equation (D-10).

The molecular constants were evaluated from  $\text{Herzberg}^{56}$  and  $\text{NBS}^{57}$  circular 467.

 $U_{s} = 1.9 \text{ mm/}\mu \text{sec and } P_{1} = 4 \text{ cm Hg give} \quad P_{4} = 11.6 \text{ atm}$   $T_{4} = 3314^{\circ}\text{K}$   $[CO] = 4.27 \cdot 10^{-5} \text{ mole/cc}$ assume initial concentration  $[H_{2}]_{0} = 10^{-3} [CO]$ from figure 32 a = 0.8

then

$$\Delta t = \frac{\alpha}{(k_d)_{t=0} [CO]} = 24 \ \mu \text{sec} \qquad (G-5)$$

This estimate is low since the fast initial rate was used but it does estimate the order of the time involved.

Due to the strong temperature dependence of  $k_d$ , this time decreases with increasing incident shock velocity and is an order of magnitude lower at  $U_s = 2.1 \text{ mm}/\mu\text{sec}$ .

#### APPENDIX H

#### EFFECT OF H-ATOMS ON CO

The results from adding 250 ppm of  $H_2$  to CO are analyzed under the assumption that the  $\phi = 7$  result in "pure CO" is due to a property of the CO molecule. The relaxation time for a gas mixture of CO + H is written as

$$\frac{1}{\tau_{\rm CO}} = \psi \left\{ \frac{1-f_{\rm H}}{\tau_{\rm CO-CO}} + \frac{f_{\rm H}}{\tau_{\rm CO-H}} \right\}$$
(H-1)

where  $\psi$  is a parameter representing the difference between relaxation times in expansion flows and behind shock waves.

## $\tau_{\rm CO}$ = relaxation time of CO in expansion, either pure or in a mixture with H-atoms.

- τ<sub>CO-CO</sub> = relaxation time of pure CO behind incident shock waves as given by Hooker and Millikan.<sup>12</sup>
- $\tau'_{CO-H}$  = relaxation time behind incident shock waves of CO dilute in an infinite bath of H-atoms.

f<sub>H</sub> = mole fraction of H-atoms.

The result obtained when  $f_{\rm H} = 0$  was  $\tau_{\rm CO} = \tau_{\rm CO-CO}/7$ , implying  $\psi = 7$ . For  $f_{\rm H} = 5 \times 10^{-4}$  the result was  $\tau_{\rm CO} = \tau_{\rm CO-CO}/12$ . If one can assume that  $\psi$  was unperturbed in this process then equation (H-1) gives

$$\frac{12}{\tau_{\rm CO-CO}} = 7 \left\{ \frac{1}{\tau_{\rm CO-CO}} + \frac{5 \cdot 10^{-4}}{\tau_{\rm CO-H}^{\dagger}} \right\}$$
(H-2)

from which

$$\frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-H}'} = \frac{1}{7} \cdot 10^4$$
 (H-3)

-95-

which should be contrasted with equation (IV-5). It can be seen that  $\tau_{\rm CO-H}$  has different values depending on which assumption is used in reducing the data. Unfortunately the question as to which is the valid assumption cannot be resolved from the expansion flow experiments described here because

# $\tau^{"}$ = relaxation time of CO in an expansion flow CO-H when infinitely dilute in a bath of H-atoms

is the same under either assumption about whether  $\phi = 7$  in 100% CO is due to impurity or not. This can be easily seen by considering (H-1) in the limit of  $f_{\rm H}$  near 1, but sufficiently less than 1 so that V-V exchange still dominates T-V exchange implying  $\psi = 7$  is still valid.

$$\frac{1}{\tau_{\rm CO-H}^{"}} = \frac{1}{\tau_{\rm CO}} \Big)_{\rm f_{\rm H}} \approx 1 = 7 \left\{ \frac{1 - f_{\rm H}}{\tau_{\rm CO-CO}} + \frac{1}{\tau_{\rm CO-CO}} \frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-H}^{'}} \right\}$$
(H-4)

neglecting the (1-f<sub>H</sub>)/ $\tau_{
m CO-CO}$  term

$$\frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-H}^{"}} = 1. \cdot 10^4$$

which is the same result deduced in the text since in that analysis  $\tau_{\rm CO-H}$  is the same in either an expansion flow or a shock wave flow.

#### APPENDIX J

## H<sub>2</sub> IN 5% CO + 95% ARGON

Here it is estimated that 0.125%  $H_2 \rightarrow 0.25\%$  H in 5% CO + 95% Ar will give  $\phi \simeq 100$ . Nozzle flow calculations for the apparatus of this thesis indicate vibrational freezing temperatures around  $2000^{\circ}$ K for  $\phi = 100$  in the specified mixture. Hence, all equations which follow are written for that temperature.

First the relaxation time for the pure CO + Ar mixture is found:

$$\frac{1}{\tau_{\rm m}} = \frac{0.05}{\tau_{\rm CO-CO}} + \frac{0.95}{\tau_{\rm CO-Ar}} = \frac{0.05}{\tau_{\rm CO-CO}} + \frac{0.95}{\tau_{\rm CO-CO}} \frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-Ar}}$$
(J-1)  
$$\tau_{\rm m} = \text{vibrational relaxation time of CO in a}$$
mixture of 5% CO + 95% Ar.

$$\tau_{\rm CO-i}$$
 = relaxation time of CO infinitely dilute in a bath of species i.

$$\frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-Ar}} \simeq 0.2, \text{ at } 2000^{\circ} \text{K, from Fig. 35.}$$
 (J-2)

with this equation (J-1) gives

$$\frac{\tau_{\rm m}}{\tau_{\rm CO-CO}}$$
 = 4.2, at 2000°K (J-3)

Now we can calculate what value of  $\phi$  will be observed when 0.25% of H-atoms are added to the mixture.

$$\frac{\phi}{\tau_{\rm m}} = \frac{1}{\tau_{\rm m}} + \frac{2.5 \cdot 10^{-3}}{\tau_{\rm CO-H}}$$
(J-4)

$$\phi = 1 + (2.5 \cdot 10^{-3}) \frac{\tau_{\rm m}}{\tau_{\rm CO-CO}} \frac{\tau_{\rm CO-CO}}{\tau_{\rm CO-H}}$$
 (J-5)

$$= 1 + (2.5 \cdot 10^{-3})(4.2)(1. \cdot 10^{4})$$
  
$$\phi = 105 \qquad (J-6)$$

	G. D. C. P. GRADE> PURIFIED		M. REAS. GRADE ANALYSIS SUPPLIED	INDEPENDENT	-₽ PURIFIED	G. D. ARGON
0 <sub>2</sub>		165	<3	35	260	110
N <sub>2</sub>			< 100			410
H <sub>2</sub>	_		< 10	<del></del> -		
co <sub>2</sub>	730	41	< 10	150	65	11
Ar	19	16	< 10	8		BALANCE
NICKLE CARBONYL		·	<del>_</del>	50		
ORGANIC PROBABLY PROPANE			<del></del> .	15		
<b>c</b> 0	BALANCE	BALANCE	BALANCE	BALANCE	BALANCE	

Table 1Mass spectrometer analyses. Concentrations are in parts-per-<br/>million (ppm). Manufacturers are General Dynamics (G. D.) and<br/>Matheson (M.). PURIFIED refers to passage of the gas through<br/>the two-trap system discussed in Section III-C. Samples were<br/>scanned from mass 2 to mass 100 with a detection threshold of<br/>4 ppm for most species (nitrogen threshold is 104 ppm).

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Fig. 11 Vibrational relaxation times for nitrogen as measured in expansion flow experiments vs stagnation temperature. Dashed line represents the measurements behind shock waves of Millikan and White<sup>60</sup> which Hurle<sup>21</sup> is in agreement with. The extremities of the solid lines give the temperature ranges covered. Sebacher<sup>9</sup> and Petrie<sup>10</sup> used Tanczos<sup>61</sup> and Blackman, <sup>16</sup> respectively, as hases for comparison.

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Fig. 2 Vibrational relaxation times for carbon monoxide as measured in expansion flow experiments vs stagnation temperature. Dashed line represents the measurements behind shock waves of Hooker and Millikan<sup>12</sup> (1100<sup>o</sup> - 2500<sup>o</sup>K) and Matthews<sup>13</sup> (2200<sup>o</sup> - 4900<sup>o</sup>K). The extremities of the solid lines give the temperature ranges covered.


Fig. 3 Filter transmission, detector response, and CO infrared emission vs wavelength. The overtone is shown a factor of 10 more intense than it is relative to the fundamental.



Fig. 4 Wave diagram for shock tunnel with gas conditions for an incident shock velocity of 2 mm/µsec into CO with hydrogen driver. The ideal test time is seen to be 0.7 milliseconds.



Fig. 5 Driver length required to prevent the first expansion wave from disturbing the untailored stagnation region vs incident shock velocity. Calculation is for a 20 foot driven tube with pure CO as the test gas and either helium or hydrogen driver gas. Driver section is 5 feet long on the shock tube used in this work.



TOP Tig. 6 Cross sectional views of the nozzle with plot of area ratio vs distance from the throat.

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Fig. 7 Vibrational temperatures in the nozzle normalized by stagnation temperature vs area ratio. For CO with stagnation conditions of  $T_4 = 3300^{\circ}$ K,  $P_4 = 11.6$  atm.



Fig. 8 Pressure and density ratio and temperature  $(T_1 = 294^{\circ}K)$  behind equilibrium incident shocks vs incident shock velocity.



Fig. 9 Conditions behind reflected shocks vs incident shock velocity. Pressure and density are normalized by their values before the incident shock,  $T_1 = 294^{\circ}K$ , and the gas model is for frozen-incident/equilibrium-reflected shocks.

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Fig. 10 Pressure ratio and temperature behind reflected shocks  $(T_1 = 294^{\circ}K)$  vs incident shock velocity for 5% CO + 95% argon. Solution is for frozen-incident/equilibrium-reflected shocks.

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Fig. 12 Photograph of the shock tunnel.



Fig. 13 Shock tunnel at the junction of the driver and driven sections showing the gas handling manifold and instruments.



Fig. 14 Pressure measured behind incident shock waves vs value calculated from measurement of shock velocity and initial pressure P<sub>1</sub>. Typical error bars are shown for two points.

c



Fig. 15 Illustration of shock velocity measurement. Oscilloscope sweep is zig-zag from top to bottom with 50 µsec between directional changes; time markers are every 10 µsec. Signal pulses from the heat transfer gauges located in the diagram are indicated on the oscillogram.



Fig. 16 End view cross section of nozzle at a window location showing one of the two optical systems.

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Fig. 17 Photograph of the optical systems.



Fig. 18 Stagnation region at end of shock tube with nozzle removed and adjustable plug installed. Two possible paths of stray radiation are shown by rays 1 and 2.



Fig. 19 Data from measurements of relaxation time behind incident and reflected shock waves. The gas was General Dynamics C.P. grade without further purification. Solid line is experimental results given by Hooker and Millikan.<sup>12</sup> The dashed line was drawn to fit the data shown here.

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Fig. 20 Number density of oxygen atoms at equilibrium behind reflected shocks divided by initial undissociated CO number-density vs incident shock velocity. Initial gas conditions are  $P_1 = 4$  cm Hg,  $T_1 = 294^{\circ}K$ .

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Fig. 21 Experimental data, diaphragm upstream of nozzle throat, oscilloscope sweep from right to left at 100  $\mu$ sec/cm. Labelling of traces is from top to bottom: a) #743, Pure CO, P<sub>1</sub> = 4 cm, U<sub>s</sub> = 1.885 mm/ $\mu$ sec. Traces 1 and 2 are first overtone emission of CO at area ratio 10 at 1 and 2 mv/cm sensitivity, respectively. Trace 3 is overtone emission from the stagnation region, 500  $\mu$ v/cm. b) #917, 5% CO + 95% Ar, P<sub>1</sub> = 10 cm, U<sub>s</sub> = 1.31 mm/ $\mu$ sec. Trace 1 is overtone emission at area ratio 35, 50  $\mu$ v/cm. Trace 3 is overtone emission at area ratio = 10. c) #810, Pure CO, P<sub>1</sub> = 8 cm, U<sub>s</sub> = 1.775 mm/ $\mu$ sec. Trace 1 is overtone emission at area ratio = stagnation region pressure at 200 psi/cm.



(a) INCIDENT SHOCK- U<sub>S</sub> = 2.285 mm / $\mu$ sec P<sub>2</sub>=0.33 atm T<sub>2</sub>=2395 °K,  $\tau_{lab}$  =8.5 $\mu$ sec,  $\tau = (\rho_2/\rho_1) - \tau_{lab} = 53.4 \ \mu$ sec



- (b) REFLECTED SHOCK- U<sub>S</sub>= 1.22 mm/ $\mu$  sec P = 3.94 atm,  $\tau_2$  = 1610 °K,  $\tau = \tau_{lab}$  =40  $\mu$  sec
- Fig. 22 Measurement of relaxation times behind incident shocks, oscilloscope sweep is from right to left. a) #448, Incident shock, pure CO b) #496, Reflected shock, pure CO.





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Fig. 24 Pressure measured behind reflected shocks, with the nozzle operating, vs incident shock velocity. Measurements with a Kistler gauge model 603A. Typical error bars are shown for two points.



Fig. 25 Temperature measured for stagnation region vs calculated temperature based on measured incident shock velocity and initial temperature.



Fig. 26 Vibrational temperature at area ratio 10 in pure CO vs incident shock velocity and stagnation temperature and pressure. The size of the error bars for these data is shown on one point.  $P_{11} = 4$  cm Hg.

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Fig. 27 Transition probabilities for CO vibrational relaxation as converted from the measured relaxation times of Hooker and Millikan<sup>12</sup>  $(\tau_{\text{CO-CO}} \text{ and } \tau_{\text{CO-H}_2})$  and this paper  $(\tau_{\text{CO-H}})$ .



Fig. 28 Radiation signal (millivolts) measured at area ratio 10 divided by mirror aperature vs incident shock velocity for different values of P<sub>1</sub> in pure CO. Optical system II, filter 30.



Fig. 29 The parameter  $\phi$  vs initial test gas pressure, P<sub>1</sub>. O - denotes data shown in Fig. 28. X - denotes calculations based on the assumption that  $\phi$  = 5 measured in pure CO at P<sub>1</sub> = 4 cm is due to an impurity whose number density concentration in the shock tube is not affected by P<sub>1</sub>.



Fig. 30 Signal divided by mirror aperture vs incident shock velocity and related stagnation conditions, for 5% CO + 95% Ar at area ratio 10. A typical error bar is shown for one point. Optical system II, filter 30.  $P_1 = 10 \text{ cm Hg}$ .

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Fig. 31 Signal divided by mirror aperture vs incident shock velocity and related stagnation conditions, for 5% CO + 95% Ar at area ratio 35. A typical error bar is shown for one point. Optical system I, filter 28.  $P_1 = 10$  cm Hg.



Fig. 32 Degree of hydrogen dissociation behind reflected shocks vs incident shock velocity for percentage of  $H_2$  in CO specified, and  $P_1 = 4$  cm Hg. Reflected shock stagnation conditions are also shown for this  $P_1$  and  $T_1 = 294^{\circ}K$ .



Fig. 33 Signal divided by mirror aperture vs incident shock velocity at area ratio 10 for pure CO with various amounts of H<sub>2</sub> added; P<sub>1</sub> = 4 cm.



Fig. 34 Vibrational temperature of CO at area ratio 10 vs incident shock velocity. Calculations are for the gas mixture CO + H<sub>2</sub> + H where  $\tau_{CO-H}$  is specified as  $\tau_{CO-H_2}/Y$ ; P<sub>1</sub> = 4 cm.



Fig. 35: Relaxation time of CO with various collision partners vs  $T^{-1/3}$ . The data for  $\tau_{CO-H}$  are derived from Fig. 34 as described in the text.