

2.

THEORY2.1 Introduction

The purpose of this chapter is to examine the conventional relaxation rate models of diatomic relaxation behind a shock or along a nozzle. The validity of these models is tested by developing a more detailed microscopic description of the diatomic relaxation processes. Simultaneously, the theoretical questions outlined in section 1.3 are to be examined.

A "ladder climbing" model of diatomic relaxation, using the vibrational Master equation, is given in section 2.2. This model is then applied to the pure N_2 experiments of Hurle et al. (1964) using the first-moment solution in section 2.3 (see also Kewley 1973). In section 2.4 the full solution of the Master equation is found by numerical integration using the algorithm of Gear (1971) (see also Kewley 1975).

Using the results of the "ladder climbing" model, the conventional rate solutions are presented in section 2.6. These solutions are used in the analysis of experiments in Chapter 3. The computer programs of Garr, Marrone, Joss and Williams (1966) and Lordi, Mates and Moselle (1966) are used for flows behind normal shocks and for nozzle expansions, respectively. A computer program to solve for nonequilibrium flow over a wedge was written for this thesis (Kewley 1974).

2.2 Diatomic Relaxation Model

The diatomic molecule is considered to be an anharmonic Morse Oscillator (MO) with dissociation and recombination occurring at the uppermost vibrational level. Rotation and translation are assumed to be in equilibrium and the above-ground electronic states are neglected. One-quantum transitions between the vibrational levels are allowed to occur;

these occur by vibration to translation energy exchange (V-T) and vibration to vibration energy exchange (V-V) between molecules. Radiative transitions, which occur for heteronuclear diatoms such as CO (Caledonia and Centre 1971), are not considered. Using these assumptions, the Master equation for the vibrational levels is constructed. This model of diatomic relaxation is of the "ladder climbing" type because dissociation is considered to be the result of an upward flux of molecules "climbing" the vibrational levels until dissociation occurs at the top level.

Previous theoretical models of diatomic relaxation can be divided into the phenomenological (Marrone and Treanor 1963 and Reinhardt 1969), the modified phase-space (Keck and Carrier 1965, Shui, Appleton and Keck 1970 and 1971, and Shui and Appleton 1971), the Monte-Carlo (Jones and Rosenfeld 1973) and the "ladder climbing" (Benson and Fueno 1962, Bray and Pratt 1967, Rich and Rehm 1967, Bray 1968 and 1970a, McElwain and Pritchard 1970 and 1971, Dove and Jones 1971 and 1972, Kiefer 1972 and 1974, Hsu and McMillen 1972, Labib, McElwain and Pritchard 1972, Wengle 1973 and Kamaratos and Pritchard 1973) types. The phenomenological model is primarily designed for vibration-dissociation coupling behind a shock wave and contains adjustable constants. It is a simple model but is not very suitable as a microscopic description of the relaxation processes. The phase-space theory, modified by incorporating the correction due to a steady-state nonequilibrium distribution in the vibrational populations of the molecules, provides an excellent model for recombination and dissociation of diatomic molecules in an inert heat bath. However this theory is not suitable for unsteady vibrational populations and is much more

complex for an undiluted diatomic gas. Similarly the Monte-Carlo theory is complex and restricted to steady-state diatomic dissociation. Of the models listed here, the "ladder climbing" type appears to be the most convenient because it is not restricted to steady-state dissociation or recombination and also provides a model for vibration-dissociation coupling.

2.2.1 The Vibrational Master Equation

The vibrational Master equation used here is similar to the one given by Dove and Jones (1971) and Wengle (1973) in that the dissociated molecules are represented by a pseudo-level. The model for the molecules is the anharmonic Morse Oscillator with vibrational energy levels given by

$$E_v = E_{10} \left((v + \frac{1}{2}) - \delta (v + \frac{1}{2})^2 \right) \quad v = 0, 1, \dots, m+1 \quad (2.2-1)$$

where E_{m+1} is the pseudo level, δ is the anharmonicity constant and E_{10} is the vibrational energy involved in the $1 \rightarrow 0$ transition. The energy difference between levels is thus

$$E_{v+1} - E_v = E_{10} (1 - 2\delta(v+1)). \quad (2.2-2)$$

Rotation and translation are assumed to be in equilibrium even though for H_2 there appear to be doubts about this assumption (Dove et al. 1973, Kamaratos and Pritchard 1973 and Pritchard 1973). Also, for convenience, only one-quantum transitions are considered, as in Dove and Jones (1971) and by Kiefer (1972), even though Wengle (1973) has shown that multi-quantum transitions can be important for O_2 , particularly for the calculation of induction times.

Using these assumptions, the Master equation for the vibrational levels can be written in the form given by Bray (1968 and 1970a) and Labib, McElwain and Pritchard (1972).

In a mass element m' , of initial density ρ_0 , initial total number density N_{T0} , atom number density N_A , inert atom number density N_I and molecule number density N_{A_2} , the time rates of change of the levels are,

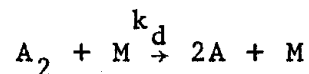
$$\begin{aligned} \frac{V_x dX_v}{N_{T0} dt} = & \sum_{s=1}^3 (B_s P_{v+1,v}) X_{v+1} - \sum_{s=1}^3 (B_s P_{v,v+1}) X_v \\ & + \sum_{s=1}^3 (B_s P_{v-1,v}) X_{v-1} - \sum_{s=1}^3 (B_s P_{v,v-1}) X_v \\ & + Z_2 \left\{ \sum_{i=1}^m (Q_{v+1,v}^{i-1,i} X_{i-1}) X_{v+1} - \sum_{i=1}^m (Q_{v,v+1}^{i,i-1} X_i) X_v \right. \\ & \left. + \sum_{i=1}^m (Q_{v-1,v}^{i,i-1} X_i) X_{v-1} - \sum_{i=1}^m (Q_{v,v-1}^{i-1,i} X_{i-1}) X_v \right\} \\ & v = 0, 1, \dots, m-1 \quad (2.2-3) \end{aligned}$$

$$\begin{aligned} \frac{V_x dX_m}{N_{T0} dt} = & \sum_{s=1}^3 (B_s P_{d,m}) X_{m+1}^2 N_{T0} - \sum_{s=1}^3 (B_s P_{m,d}) X_m \\ & + \sum_{s=1}^3 (B_s P_{m-1,m}) X_{m-1} - \sum_{s=1}^3 (B_s P_{m,m-1}) X_m \\ & + Z_2 \left\{ \sum_{i=1}^m (Q_{m-1,m}^{i,i-1} X_i) X_{m-1} - \sum_{i=1}^m (Q_{m,m-1}^{i-1,i} X_{i-1}) X_m \right\} \\ & (2.2-4) \end{aligned}$$

$$\frac{V_x dX_{m+1}}{N_{T0} dt} = \sum_{s=1}^3 (B_s P_{m,d}) X_m - \sum_{s=1}^3 (B_s P_{d,m}) X_{m+1}^2 N_{T0} / V_x, \quad (2.2-5)$$

where $B_s = Z_s N_s / N_T$ and $s=1,2,3$ corresponds to inert atoms, molecules and atoms, $V_x = \rho_0 / \rho_x$ and $X_v = N_v / N_{T0}$. For the heat bath solutions Equations 2.2-3, 4 and 5 are integrated with $V_x = 1$.

The dissociation rate equation for the reaction



is

$$-\frac{dN_{A_2}}{dt} = k_d N_T (N_{A_2} - (N_A)^2 / K(T)) = N_{T0} \frac{dX_{m+1}}{dt} \quad (2.2-6)$$

and so k_d can be calculated from the numerical solutions.

The vibrational relaxation rate equation is the Landau-Teller equation,

$$\frac{de_v}{dt} = \frac{e_v(T) - e_v}{\tau_v} \quad (2.2-7)$$

where $e_v = N_{T0} \sum_{i=1}^m (E_i - E_0) X_i$ is the vibrational energy and $e_v(T)$ is the equilibrium vibrational energy at the translational temperature T . The equilibrium vibrational level populations \tilde{X}_v at T are found by

$$\tilde{X}_v = N_T \exp(-E_v/kT) / (N_{T0} Q_{vib}(T)) \quad (2.2-8)$$

where $Q_{vib}(T)$ is the vibrational partition function and k is Boltzmann's constant. Thus τ_v can be found using Eq.2.2-7. Therefore the relaxation rate parameters, k_d and τ_v , can be found once a set of transition probabilities is given.

2.2.2 Transition Probabilities

The probabilities are required for V-V and V-T transitions. $Q_{v+1,v}^{i-1,i} = (v+1)i Q(i,v,T)$ is the probability of V-V energy exchange between two molecules on collision while $P_{v+1,v} = (v+1)P(v,T)$ is the probability of V-T energy exchange between two molecules or one molecule and atom on collision. The Harmonic Oscillator gives $Q(i,v,T) = Q_{10}^{01}$ and $P(v,T) = P_{10}$ but here the analytic forms for the MO given by Bray (1968), which are Keck and Carrier's (1965) modification of the SSH theory (Herzfeld and Litovitz 1959), are used.

$$\begin{aligned} P(v,T) &= P(T) F(y_{v+1,v}) / (1 - \delta(v+1)) \\ Q(i,v,T) &= \{ Q(T) F(y_{v+1,v}^{i-1,i}) / ((1 - \delta(v+1))(1 - \delta(i))) \} \\ &\quad \text{for } i \leq v+1 \\ &= \{ \} \exp((E_{v+1} + E_{i-1} - E_i - E_v) / kT) \\ &\quad \text{for } i > v+1 \end{aligned}$$

where F is the adiabaticity factor, whose arguments are

$$y_{v+1,v} = \left(\frac{1}{2}\right)^{3/2} (\theta'/T)^{1/2} (1-2\delta(v+1))$$

$$y_{v+1,v}^{i-1,i} = 2\delta \left(\frac{1}{2}\right)^{3/2} (\theta'/T)^{1/2} |v+1-i|. \quad (2.2-10)$$

The empirical fit of Keck and Carrier (1965) for F is

$$F(y) = \frac{1}{2} \{3 - \exp(-2y/3)\} \exp(-2y/3). \quad (2.2-11)$$

These analytic forms are convenient because the probabilities have to be continually re-evaluated as the temperature changes behind the normal shock and along the nozzle. The transition probability functions given here have also been used by Rich (1971) for an electrical CO laser and McKenzie (1972) for the gas dynamic CO-N₂ laser.

Through the relation,

$$\theta' = 0.8153 \tilde{W} \theta_v^2 L^2 \quad (2.2-12)$$

where \tilde{W} is the reduced molecular weight, the probability calculations depend upon knowing the interaction potential parameter, L , for the exponential potential

$$U = U_0 \exp(-r/L).$$

The value of L is very important for *a priori* transition probabilities but it is difficult to say what value it should take for the various collision partners. For example, consider H₂ in a heat bath of Ar which was examined by Dove and Jones (1971 and 1972), Shui and Appleton (1971) and Kiefer (1972) who use a value of L of 0.25, 0.347 and 0.247 Å, respectively. Dove and Jones (1972) chose L to give agreement between an *a priori* calculation of P_{10} and the experimental value from Kiefer and Lutz (1966b). Kiefer (1972) deduced a value for L from the experimental temperature dependence of τ_v . Alternatively, Shui and Appleton's (1971) value of L is deduced from an empirical

formula given in Shui, Appleton and Keck (1970), using beam scattering measurements for confirmation. The sensitivity of recombination rate coefficients to L is shown in Shui and Appleton (1971) who incidentally get good agreement with experiment with their value of L . Whenever possible, the value of L used in the modified phase-space methods (see also Shui, Appleton and Keck 1971 for a list) is used. Values are also to be found in Benson and Berend (1966).

To ensure that τ_v has the right magnitude compared to experiments the value of $P(1,T) = P_{10}$ is found from experiments using

$$P_{10} = 1/(Z N_T \tau_v (1 - \exp(-\theta_v/T))), \quad (2.2-13)$$

where $Z = 4\sigma^2(\pi kT/2\mu)^{1/2}$, σ is the hard sphere collision diameter (Hirschfelder, Curtiss and Bird 1954 and Dorrance 1962) and μ is the reduced mass.

The value of Q_{10}^{01} is calculated from the theory of Rapp and Englander-Golden (1964) and Rapp (1965) given by Fisher and Kummler (1968) and Kiefer (1972):

$$Q_{10}^{01} = q \cdot 610 \cdot T \cdot 0.04/W_A \cdot \theta_v^2 \cdot L^2 \quad (2.2-14)$$

where W_A is the molecular weight of the atom A and q is a factor employed in the calculations here to vary the magnitude. The normal value of Q_{10}^{01} is found with q equal to one. A comparison with experiment is given by Rapp (1965).

With $P_{v+1,v}$ and $Q_{v+1,v}^{i-1,i}$ known and $P_{m,d} = P_{m,m+1}$ (as in Dove and Jones 1971), the reverse probabilities are found by "detailed balancing":

$$P_{v,v+1} = P_{v+1,v} \exp(-(E_{v+1} - E_v)/kT)$$

$$Q_{v,v+1}^{i,i-1} = Q_{v+1,v}^{i-1,i} \exp(-(E_{v+1} + E_{i-1} - E_v - E_i)/kT)$$

$$P_{d,m} = P_{m,d} \exp(-E_m/kT) 4/(K(T)Q_{vib}(T)) \quad (2.2-15)$$

A list of the necessary data obtained from Kiefer (1972), Shui and Appleton (1971), Hirschfelder et al. (1954) and Dorrance (1962) for studying H_2 in Ar follows. An example of the vibrational transition probabilities for H_2 at 5000K and 1 atm is given in Figure 2.1

$$E_{10}/k = 6113K, \delta = 0.0278, m = 15, \theta_d = 51960K,$$

$$p\tau(H_2-H_2) = 3.9 \times 10^{-10} \exp(100T^{-1/3}) \text{ atm-sec}, p\tau(H_2-Ar)$$

$$= 4p\tau(H_2-H_2), p\tau(H_2-H) = 6.43 \times 10^{-10} \exp(81T^{-1/3}) \text{ atm-sec},$$

$$L(H_2-H_2) = 0.338\overset{\circ}{\text{A}}, L(H_2-Ar) = 0.347\overset{\circ}{\text{A}}, L(H_2-H) = L(H_2-H_2),$$

$$\sigma(H_2-H_2) = 2.93\overset{\circ}{\text{A}}, \sigma(H_2-Ar) = 3.15\overset{\circ}{\text{A}} \text{ and } \sigma(H_2-H) = 2.65\overset{\circ}{\text{A}}.$$

2.3 First-Moment Solution

In this section the first-moment solution of the vibrational Master equation, with no dissociation, is given and used to investigate the sodium-line reversal experiments of Hurle et al. (1964) in pure N_2 . The method of solution follows Bray (1968 and 1970a) in that the rate of change of the vibrational "temperature" is a function of both the V-T energy exchanges and the distortion of the vibrational level distribution, by V-V energy exchanges, due to the changing translational temperature.

The advantage of this type of solution, over the one given in section 2.4, is that the calculation is quicker than numerically integrating the Master equation which is stiff (Treanor 1966 and McElwain and Pritchard 1971). A system of differential equations is said to be stiff if the eigenvalues are different by orders of magnitude.

2.3.1 Method

For a pure diatomic gas, with no dissociation occurring,

in a heat bath, the vibrational Master equations become

$$\begin{aligned} \frac{dX_v}{ZN_{T0} dt} &= P_{v+1,v} X_{v+1} - P_{v,v+1} X_v + P_{v-1,v} X_{v-1} - P_{v,v-1} X_v \\ &+ \sum_{i=1}^m (Q_{v+1,v}^{i-1,i} X_{i-1} X_{v+1} - Q_{v,v+1}^{i,i-1} X_i X_v) \\ &+ \sum_{i=1}^m (Q_{v-1,v}^{i,i-1} X_i X_{v-1} - Q_{v,v-1}^{i-1,i} X_{i-1} X_v) \end{aligned} \quad (2.3-1)$$

$$v = 0, 1, \dots, m-1$$

$$\frac{dX_m}{ZN_{T0} dt} = P_{m-1,m} X_{m-1} - P_{m,m-1} X_m + \sum_{i=1}^m (Q_{m-1,m}^{i,i-1} X_i X_{m-1} - Q_{m,m-1}^{i-1,i} X_{i-1} X_m) \quad (2.3-2)$$

Using these equations, expressions for the vibrational level populations are derived and used in conjunction with the first-moment equation.

By summing up to a level k one obtains

$$\sum_{v=0}^k \frac{dX_v}{ZN_{T0} dt} = P_{k+1,k} X_{k+1} - P_{k,k+1} X_k + \sum_{i=1}^m (Q_{k+1,k}^{i-1,i} X_{i-1} X_{k+1} - Q_{k,k+1}^{i,i-1} X_i X_k) \quad (2.3-3)$$

if $\frac{dX_v}{dt} = 0$, then

$$X_{k+1} = X_k \left(\sum_{i=1}^m (Q_{k,k+1}^{i,i-1} X_i) + P_{k,k+1} \right) / \left(\sum_{i=1}^m (Q_{k+1,k}^{i-1,i} X_{i-1}) + P_{k+1,k} \right). \quad (2.3-4)$$

Following Gordiets, Osipov and Shelepin (1971) Equation 2.3-4 can be rewritten as

$$X_{k+1} = X_k \exp(\theta_v 2\delta k/T) \phi_k \exp(-\theta_v/Y) \quad (2.3-5)$$

where $\phi_k = \left\{ \sum_{i=1}^m Q(i,k,T) \exp(-\theta_v 2\delta(i-1)/T) i X_i^0 + P(k,T) \exp(-\theta_v(1-2\delta)/T) \right\} \exp(\theta_v/Y) / \left(\sum_{i=1}^m Q(i,k,T) i X_{i-1}^0 + P(k,T) \right)$ and $\phi_0 = 1$.

By recursion, the steady-state population is then given by

$$X_n(ss) = X_o \exp[-n(\theta_v/Y - (n-1)\theta_v\delta/T)] \prod_{k=0}^{n-1} \phi_k \quad (2.3-6)$$

where Y is the $1 \rightarrow 0$ vibrational temperature. Thus the steady-state solution of the vibrational level distribution is found in terms of X_i^o , Y and X_o . $\sum_{i=0}^m X_i = 1$ determines

X_o and X_i^o can be the previous X_i in an iteration procedure, starting with $\phi_i = 1$, or a good approximation of the final X_i ; Y is specified. Equation 2.3-6 has the same form as Eq.(5) of Center and Caledonia (1972) and is actually more specific as it has no unknown functions. With $\phi_i = 1$, the distribution is similar to that given by Treanor et al. (1968) and for $\phi_i = \exp(\theta_v 2\delta/Y)$ the distribution is the same. Figure 2.2 shows the vibrational level distributions for pure N_2 with $Y = 3000K$ and T varying from 4000 to 800K (compare with Fig. 3 of Bray 1968).

If $\frac{dX_v}{dt} \neq 0$ then

$$X_{k+1} = X_k \exp(\theta_v 2\delta k/T) \phi_k \exp(-\theta_v/Y) + \beta_{k+1} \quad (2.3-7)$$

where

$$\beta_{k+1} = \left[\sum_{v=0}^k \frac{dX_v}{Z N_{T0} dt} \right] (k+1)^{-1} \left[\sum_{i=1}^m Q(i,k,T) i X_{i-1}^o + P(k,T) \right]^{-1}.$$

By recursion, the unsteady population is given by

$$X_n = X_n(ss) + \sum_{j=0}^{n-1} \beta_{n-j} \exp(-j(\theta_v/Y - (n-(j+1)/2)\theta_v\delta/T)) \prod_{i=1}^j \phi_{n-i}. \quad (2.3-8)$$

The first-moment equation is obtained by multiplying the Master equations 2.3-1 and 2 by v and summing over all the vibrational levels. It is

$$\frac{1}{Z N_{T0}} \sum_{v=0}^m v \frac{dX_v}{dt} = - \sum_{v=0}^m (P_{v,v-1} X_v - P_{v-1,v} X_{v-1}).$$

The V-V terms cancel out because one-quantum transitions conserve vibrational quanta (see Hsu and McMillen 1970 for a proof). However this does not mean that vibrational energy is conserved during V-V energy exchanges.

Following Bray (1968 and 1970a), it is assumed that $X_v = X_v(Y, T)$ and so

$$\frac{dX_v}{dt} = \left(\frac{\partial X_v}{\partial Y} \right)_T \frac{dY}{dt} + \left(\frac{\partial X_v}{\partial T} \right)_Y \frac{dT}{dt} \quad (2.3-10)$$

where higher order derivatives $d^n T/dt^n$ are neglected. By substituting this equation into the first moment equation, dY/dt is found:

$$\frac{dY}{dt} = (-ZN_{T0} \sum_{v=0}^m (P_{v,v-1} X_v - P_{v-1,v} X_{v-1}) - \frac{dT}{dt} \sum_{v=0}^m v \left(\frac{\partial X_v}{\partial T} \right)_Y) / \sum_{v=0}^m v \left(\frac{\partial X_v}{\partial Y} \right)_T \quad (2.3-11)$$

Using this equation with a specified Y, T, N_{T0} and dT/dt , the variation of Y in a nozzle expansion can be found. The values of the derivatives are found by perturbing Y and T where Eq. 2.3-8 is used to find X_v . Figure 2.2 shows the vibrational level distributions for pure N_2 with $Y = 3000K$ and $T = 1000K$ for various values of dT/dt (compare with Fig. 1 of Bray 1970a). The necessary data for N_2 , from Bray (1968), is $\theta_v = 3395K$, $\delta = 6.217 \times 10^{-3}$, $m = 47$, $P(T) = 1.07 \times 10^{-4} T \text{ sec}^{-1}$, $Q(T) = 3.7 \times 10^{-6} T \text{ sec}^{-1}$, $\theta' = 5.39 \times 10^6 K$ and $\sigma(N_2-N_2) = 3.35 \text{ \AA}$.

2.3.2 Comparison with Experiment

Using dY/dt in a Runge-Kutta nozzle integration (see section 2.6.3 and Lordi et al. 1966) theoretical calculations of Y for the shock tunnel experiments of Hurle et al. (1964) in pure N_2 are made. $Y = T$ is assumed until the vibrational

sudden freeze criterion (Phinney 1964, Bray 1970b and section 2.6.3), using τ_s from shock tube experiments (Millikan and White 1963a and Appleton 1967), is satisfied. For thermodynamic equilibrium calculations using the vibrational energy, an effective vibrational temperature T_v is used. T_v is defined by

$$\sum_{v=0}^m v X_v = 1/(\exp(\theta_v/T_v)-1) \quad (2.3-12)$$

Figures 2.3 and 2.4 show the results of the calculations. Just as these calculations were being completed, MacDonald (1972) showed that the SLR experiments need to be reinterpreted when Y is greater than T . The new interpretation of Hurle et al.'s measurements according to MacDonald is also shown in the figures. The vibrational energy relaxation rate corresponds to about $\tau_s/1.4$ or $\phi = 1.4$ while the Y rate corresponds to $\tau_s/3$ or $\phi = 3$. These results appear to confirm the theory of Bray (Bray 1968 and 1970a and Bray and Pratt 1970).

The results obtained here, for N_2 and by Center and Caledonia (1972), for CO, indicate that anharmonicity effects account for the observed behaviour of N_2 and CO vibrational relaxation in a nozzle. The electron-beam experiments in N_2 (see Hurle 1971) have yet to be compared with detailed calculations of the type given here and by Center and Caledonia (1972).

2.4 Full Solution

The vibrational Master equation, including dissociation, is numerically integrated in a heat bath, behind a normal shock and along a nozzle. From these solutions the vibrational excitation, dissociation, vibrational de-excitation and

recombination rates are found.

For H_2 the value of m is 15, which is smaller than m for N_2 and O_2 , and so H_2 is used as the model for diatomic molecules because the computing time is lowest. Some calculations for N_2 are also made. Exact agreement with experimental results for H_2 relaxation rates is not the aim of this calculation, and consequently rotation and translation are assumed to be in equilibrium; even though for H_2 there appear to be doubts about this assumption (Dove, Jones and Teitelbaum 1973, Kamaratos and Pritchard 1973 and Pritchard 1973).

For the heat bath solutions Equations 2.2-3, 4 and 5 are integrated with $V_x = 1$. Using dx/u instead of dt in the Master equation and the following three differential equations, which determine the temperature, density and flow velocity, the shock wave and nozzle solutions are found by integrating with respect to distance x . Following Labib et al. (1972) the equations are

$$\begin{aligned} \frac{dT}{Tdx} = & \left(\frac{dN_T}{N_T dx} - \frac{2\bar{\epsilon}_u}{kT} \frac{dA}{Adx} + \left\{ \frac{2\bar{\epsilon}_u}{kT} - 1 \right\} \left\{ -\frac{\theta_d}{2T} \frac{dN_H}{N_T dx} - \frac{3}{2} \frac{dN_T}{N_T dx} \right. \right. \\ & \left. \left. - \frac{R_{H_2}}{kT} \frac{dN_{H_2}}{N_T dx} - \frac{\sum \epsilon_i}{kT} \frac{dN_i}{N_T dx} \right\} \right) / \left(\left\{ \frac{2\bar{\epsilon}_u}{kT} - 1 \right\} \left\{ \frac{3}{2} + \frac{1}{k} \left(\frac{dR_{H_2}}{dT} \right) \frac{N_{H_2}}{N_T} \right\} - 1 \right) \end{aligned} \quad (2.4-1)$$

$$\frac{d\rho}{\rho dx} = \left(\frac{dT}{Tdx} + \frac{dN_T}{N_T dx} - \frac{2\bar{\epsilon}_u}{kT} \frac{dA}{Adx} \right) / \left(\frac{2\bar{\epsilon}_u}{kT} - 1 \right) \quad (2.4-2)$$

$$\frac{du}{udx} = - \left(\frac{d\rho}{\rho dx} + \frac{dA}{Adx} \right) \quad (2.4-3)$$

where $\bar{\epsilon}_u = m'u^2/2N_T$, A is the cross-sectional area of the stream tube (constant for a normal shock), $dN_H = N_{TO} dX_H = N_{TO} 2dX_{m+1}$, $dN_{H_2} = -N_{TO} dX_{m+1}$, $dN_i = N_{TO} dX_i$, $\epsilon_i = E_i - E_0$ and R_{H_2} is the rotational energy.

Normal methods of numerical integration such as the Runge-Kutta and Adams predictor-corrector are not suitable for the solution of the Master equation because the equations are stiff. However the algorithm of Gear (1971) was written especially for stiff differential equations and so it is used here. In the following sub-sections vibrational relaxation is studied first and then simultaneous vibrational and chemical relaxation is allowed. The effect of V-V transitions on the solutions is found by multiplying the normal value of Q_{10}^{01} by various values of q (see Equation 2.2-14). Using the A.N.U. Univac 1108 computer, the typical time for the non-isothermal solutions for H_2 is 5 minutes. The necessary data for H_2 is given in section 2.2.2.

2.4.1 Heat Bath

A detailed investigation of the relaxation rates is left for the shock and nozzle solutions, in sections 2.4.2 and 3, respectively. However some effects of V-V transitions and a discussion of the linear rate law are presented here.

The heat bath solution has been presented previously for vibrational relaxation by Dove and Jones (1971) for excitation of H_2 in Ar without V-V transitions and by Hsu and McMillen (1972) for de-excitation of N_2 including V-V transitions. Dove, Jones and Teitelbaum (1973) have included rotational levels in the Master equation for H_2 in Ar and have shown evidence for vibration-rotation coupling. Rich and Rehm (1967) presented analytic solutions for the case of equi-distant vibrational energy level spacing, i.e. a Truncated Harmonic Oscillator (THO), with and without V-V transitions for a general diatomic gas. However none of these references has presented heat bath solutions for both

vibrational excitation and de-excitation, with and without V-V transitions, for a gas of anharmonic oscillator molecules; this is done here.

Figure 2.5 shows the time evolution of the H_2 levels at 5000K and 1 atm, from an initial population in equilibrium at 300K, with the levels eventually reaching a Boltzmann distribution at 5000K. The V-V transitions have the effect of increasing the relaxation rates of the lower levels and decreasing the rates for the upper levels. For de-excitation from equilibrium at 10000K to 5000K at constant pressure of 1 atm, see Figure 2.6, the V-V transitions have the same effect.

The heat bath solution for dissociation has been presented previously by McElwain and Pritchard (1971) for H_2 in He, Dove and Jones (1971) for H_2 in Ar and Wengle (1973) for H_2 and O_2 in Ar, all without V-V transitions. V-V transitions were included by McElwain and Pritchard (1970) for H_2 in He. Recombination in a heat bath without V-V transitions has also been presented by McElwain and Pritchard (1971). These references serve as a check on the features of the calculations presented here.

Figure 2.7 shows the time evolution of the H_2 levels at 5000K and 10 atm, from an initial population in equilibrium at 300K, with the levels eventually reaching vibrational and chemical equilibrium at 5000K. The population of the highest level of the molecule now represents half the atom population. It is clearly seen that dissociation occurs before a Boltzmann distribution is reached among the upper levels. This is found to become more pronounced as the temperature is increased. The relaxation of upper levels

is decreased by V-V transitions as found for vibrational relaxation. Thus the rate of increase of the atoms is delayed, i.e. the induction time for dissociation is increased by V-V transitions. Recombination from 10000K and 10 atm with a mole fraction of H_2 equal to 10^{-8} , shown in Figure 2.8, appears to show that V-V transitions have no effect on the relaxation rates of the levels. Starting from the top, the levels increase in population until they are nearly in equilibrium then recombination becomes effective.

The linear rate law assumes that, for H_2 and H in Ar

$$k_d = k_d^{Ar} \frac{N_{Ar}}{N_T} + k_d^{H_2} \frac{N_{H_2}}{N_T} + k_d^H \frac{N_H}{N_T} \quad (2.4-4)$$

Kiefer (1972) using a steady-state solution has shown that this equation can fail for H_2 and H in Ar and for O_2 and O in Ar but this conclusion was sensitive to the V-T transition rates of H and O. The vibrational relaxation rate of H_2 by H has yet to be measured definitely (see Breen, Quy and Glass (1973b) for an attempt) so no attempt was made here to check the rate law for H_2 and H mixtures. The relaxation rate used is the value given by Kiefer (1972) using Millikan and White's (1963b) correlation. For H_2 and Ar mixtures the initial dissociation rate with and without V-V transitions is shown on Figure 2.9 for 5000K. The rate coefficient k_d^{Ar} calculated from 4000K to 8000K is found to be 1.5 times higher at 4000K and equal at 8000K to k_d^{Ar} determined experimentally by Breshears and Bird (1973a). Their measurement of $k_d^{H_2}$ was made assuming the linear rate law for mixtures up to 20% H_2 in Ar and according to Figure 2.9 this would lead to an overestimation of $k_d^{H_2}$. The linear rate law appears to fail even without V-V transitions.

However if the normalised V-T transition probabilities, $P(v,T)/P_{10}$, for H_2 -Ar collisions are used for H_2 - H_2 collisions the rate law, without V-V transitions, is linear, in agreement with McElwain and Pritchard (1970). For this case it is interesting to note that $p\tau(H_2\text{-Ar})/p\tau(H_2\text{-}H_2)$ is nearly equal to $k_d^{H_2}/k_d^{Ar}$.

These heat bath calculations show that the model is suitable for describing the relaxation rates and can therefore be used for the shock and nozzle solutions. The effect of V-V transitions on the relaxation rates of the levels, on the induction time and on the rate law has been clarified. The linear rate law appears to fail even for mixtures of diatomic molecules and inert atoms, as the concentration of the inert atoms is reduced, although the V-T transition probabilities need to be known more accurately before a definite conclusion can be reached.

2.4.2 Normal Shock

The above method may now be applied to calculations of vibrational excitation and dissociation in the flow after a normal shock. This has so far only been done for the isothermal case. Experiments in N_2 by Appleton (1967) and Hanson and Baganoff (1970) and CO by Hanson (1971) have shown evidence of "hooks" on Landau-Teller plots of $\log_{10}(p\tau_v(\text{atm-sec}))$ against $T^{-1/3}$. Simpson (1973) suggests that the shock tube evidence for this effect is divided and not very conclusive but calculations here, Figure 2.10, for H_2 show a tendency to "hooks" or an increase in the vibrational excitation rate as equilibrium is approached. Calculations are made for an initial condition of 300K and 5 torr at the four shock speeds of 8, 10, 12 and 14 km/sec with τ_v de-

terminated from Equation 2.2-7. No dissociation is allowed to occur for these solutions. The V-V transitions cause the relaxation rate to increase as equilibrium is approached with the increase becoming larger for q equal to 100. For slower shocks there is less tendency for "hooks" which is in agreement with the experiments. The "hooks" may be more pronounced if multi-quantum transitions were allowed but allowing only one-quantum transitions seems sufficient in showing this effect.

This acceleration of relaxation appears to contradict the results of Rich and Rehm (1967) who showed, in a heat bath, that V-V transitions increase the accuracy of the vibrational energy relaxation Equation 2.2-7. However it must be noted that for their model there is no energy lost to, or gained from, translation during a V-V energy exchange and so V-V transitions cannot directly influence the vibrational energy relaxation rate. In agreement with Rich and Rehm, heat bath calculations using the present method with $\delta = 0$ (THO) show no acceleration of relaxation. Checks are made, considering V-V transitions only, to ensure that in both the MO and THO calculations vibrational quanta are conserved and that no energy is lost to, or gained from, translation for the THO. The hook effect increases the rate by a factor of 1.7 at most and temperatures have to be near or above θ_v for it to be significant. If indeed the "hooks" are real then possibly they could be used to deduce the self V-V transition probabilities for a diatomic molecule. The jitter which appears on Figure 2.10 and other figures is due to recalculating the transition probabilities at say every 50K rather than at every integration step.

Calculations of vibrational excitation after normal

shocks in N_2 are shown in Figure 2.11. Shocks of speeds 4.5, 4.0, 3.5 and 3.0 km/sec are considered in N_2 at 300K and 5 torr. This covers the range of temperatures at which Appleton (1967) and Hanson and Baganoff (1970) have measured the vibrational excitation rate. The data, from section 2.3.1, Millikan and White (1963a), Benson and Berend (1966) and Dorrance (1962) used for the calculation is listed:
 $E_{10}/k = 3395K$, $\delta = 6.217 \times 10^{-3}$, $m = 43$, $p\tau(N_2-N_2) = 5.7 \times 10^{-12} \exp(234.9T^{-1/3})$ atm-sec, $L(N_2-N_2) = 0.263\text{\AA}$ and $\sigma(N_2-N_2) = 3.75\text{\AA}$.
 As found for H_2 , there is a deviation away from the expected rate which is caused by including V-V transitions in the Master equation. The deviation again increases with temperature. These results seem to indicate that the "hooks" observed by Appleton (1967) and Hanson and Baganoff (1970) and discounted by Simpson (1973) may be real.

The dissociation rate coefficient, k_d , for three shocks, with initial conditions of 300K and 5 torr and shock speeds of 10, 12 and 14 km/sec, is shown in Figure 2.12. For comparison the value of $k_d^{H_2}$ found by Breshears and Bird (1973a) is also plotted. The normal V-V transition probabilities have little effect on k_d and a value of q equal to 100 is needed to increase k_d by a factor of two. These results show that the set of transition probabilities for H_2-H gives a value of k_d^H too small to be resolved because the profiles of the faster shocks merge with those of the slower shocks.

In diatomic dissociation studies it is customary to express k_d in the form given by Equation 1.2-6, $CT^{-n} \exp(-\theta_d/T)$, where n is expected to be less than or equal to 1.5. Here a value of n between 1 and 1.5 fits k_d over a temperature

range of 3000K to 6000K, which is in reasonable agreement with Sutton (1962) who found n to be 1. It has been suggested by Kiefer (1972) that values of n greater than 1.5 found for undiluted diatomic gases (see section 1.2.2) are caused by V-V transitions but this is not apparent for H_2 .

Calculations for nitrogen dissociation behind a shock wave are not practical because of the excessive amount of computer time required.

2.4.3 Nozzle Flow

The nozzle flow is represented by flow along a conical nozzle, with a 7.5 half angle and a 0.318 cm throat diameter; the calculation beginning down-stream of the throat where the Mach number is around 1.04. The flow conditions at the start of the calculations are found using the computer program of Lordi et al. (1966). Contrary to Labib et al. (1972), R_{H_2} was assumed to be equal to kT for both the shock and nozzle solutions because this is the value assumed by the conventional nozzle program. Following Labib et al. (1972), the vibrational populations were assumed to be still in equilibrium at the start point.

Figure 2.13 shows the results of a nozzle calculation with the reservoir conditions of 3000K and 50 atm. It can be seen that the vibrational relaxation rate for H_2 along a nozzle follows the experimental value down to a temperature of 860K although it is a factor of 1.4 faster. The effect of V-V transitions on the rate was negligible even for q equal to 100. Similar results for N_2 were found in section 2.3.2 in that the vibrational energy relaxation rate was independent of V-V transitions while the vibrational "temperature" rate was not. Since the vibrational energy is

determined mainly by the first level population, the temperature T_{01} (=Y) of the first level (defined by $X_1/X_0 = \exp(-\epsilon_1/T_{01})$) is a good guide to the vibrational energy in the gas. In Figure 2.14, T_{01} and T_∞ (free stream translational temperature) are plotted against distance along the nozzle. It can be seen that T_{01} freezes at around 1500K with no V-V transitions and at a slightly lower value with them included. This effect of V-V transitions in reducing T_{01} is in agreement with the results of section 2.3.2. The observed freezing temperature is in approximate agreement with numerical calculations of vibrational de-excitation using Lordi et al. (1966) and the vibrational sudden freeze criterion (Phinney 1964, Bray 1970b and section 2.6.3) for the same nozzle flow.

For recombination of H_2 along a nozzle, with reservoir conditions of 5000K, 6000K and 7000K at 200 atm, the rate coefficient k_d is virtually identical to the normal shock value in the range 6000K to 2700K. This agrees with the results of Labib et al. (1972) showing that the rate quotient law (Eq. 1.2-5) is valid, i.e. $k_d = k_r K(T)$. Figures 2.15a, b and c show T_{01} , T_∞ and α , the atom mass fraction, plotted against distance along the nozzle for the three different reservoir conditions. Contrary to the solution without chemical effects T_{01} is higher with V-V transitions than without them. When the lowest levels freeze out the vibrational relaxation rate becomes negative, in agreement with Labib and Pritchard (1974) who observed the same effect for H_2 in He. Since k_d is found for temperatures down to 700K an approximate expression for k_d , to be used in the conventional nozzle program, is fitted to the results.

The expression is $k_d = 8.1 \times 10^{21} T^{-2} \exp(-\theta_d/T) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$. Considering the Master equation, the vibrational relaxation rate is assumed to be uncoupled from recombination and so the sudden freeze criterion is used in the conventional nozzle calculation. The results in Figure 2.15 show good agreement between the two solutions for α and T_{01} . Calculations with 30 and 40 degree nozzles, for 7000K and 200 atm, give qualitatively similar results to those presented in Figure 2.15c with higher frozen values of α and T_{01} .

2.5 Summary of Theoretical Results

The model for diatomic relaxation rates used here seems to give an adequate description of vibrational and chemical relaxation even though it is still incomplete because it neglects multi-quantum transitions, rotation effects and dissociation from vibrational levels other than the top pseudo-level. The questions, 1 and 2 outlined in section 1.3.1, and 1 and 2 outlined in section 1.3.2, are examined using the first-moment solution (section 2.3) or by numerical integration (section 2.4) of the Master equation. Question 3 of section 1.3.2 will be examined in Chapter 3.

It is found that vibration to vibration (V-V) energy exchanges cause the induction time for dissociation of H_2 to be increased; suggest that the linear rate law, for H_2 and Ar mixtures, fails for a H_2 mole fraction above 20%; give an acceleration of vibrational excitation as equilibrium is approached for H_2 and N_2 ; cause the vibrational temperature, T_{01} or Y , to be lower than the value found without V-V transitions for vibrational de-excitation in nozzle flows of H_2 and N_2 , and conversely for recombination of

H₂ along a nozzle.

The vibration to translation (V-T) energy exchanges for solutions in H₂ appear to be the main mechanism of diatomic relaxation rates because the calculated rate coefficients are within the scatter of experimental results; although this is sensitive to the possible values of L. The solutions show that V-T transitions can also cause the linear rate law, for H₂ and Ar mixtures, to fail if the sets of normalised V-T transition probabilities for H₂-H₂ and H₂-Ar collisions are different from each other, and that they are the main cause of T₀₁ freezing in the nozzle.

The use of conventional nozzle flow programs, with shock-tube-determined dissociation and vibrational excitation rates, to solve for recombining and vibrationally de-exciting flows, appears to be valid for the cases considered.

2.6 Conventional Methods of Solving Relaxation Rate Problems

In the preceding sections a detailed microscopic description of the diatomic relaxation processes has been presented. Detailed accounts of the methods for solving relaxing flow problems are available in the references to be quoted. The present section only gives an outline of the method sufficient for present purposes. The specific problems to be considered here are for relaxation behind a normal shock, along a nozzle and over a wedge. The conventional thermodynamic model used by these methods is also given.

2.6.1 Thermodynamic Model

In Chapters 1 and 2, some relevant thermodynamic quantities have already been mentioned and included in the theoretical Master equation solutions.

For chemical relaxation, in a mixture of atoms and di-

atomic molecules, with translational, rotational and vibrational equilibrium, expressions for the partition functions, internal energies, specific heats and equilibrium constant are listed here. (See Chapter IV and V of Vincenti and Kruger 1965).

The partition functions for a species $i (=A_{n_i})$ are:

$$Q_i = \prod_j Q_{j,i} \quad (2.6-1)$$

$$Q_{Tr,i} = V(2\pi m_i kT/h^2)^{3/2} \quad (2.6-2)$$

where V is the volume, m_i is the mass and h is Planck's constant

$$Q_{Rot,i} = (T/\sigma \theta_{R,i})^{(n_i-1)} \quad (2.6-3)$$

where $\theta_{R,i}$ is the characteristic rotational temperature and $\sigma = 2$ for homonuclear, $= 1$ for heteronuclear molecules.

$$\begin{aligned} Q_{vib,i} &= (n_i-1) \sum_v \exp(-E_{v,i}/kT) = Q_{vib,i}(T) \quad (2.6-4) \\ &= (n_i-1)/(1-\exp(\theta_{v,i}/T)) \text{ for a simple HO (SHO)} \end{aligned}$$

$$Q_{El,i} = \sum_l g_{l,i} \exp(-E_{l,i}/kT) \quad (2.6-5)$$

where $g_{l,i}$ is the degeneracy of electronic level l with energy $E_{l,i}$. The internal energies per unit mass of a

species i are:

$$e_i = \sum_j e_{j,i} = \frac{RT^2}{W_i} \frac{\partial \ln Q_i}{\partial T} \quad (2.6-6)$$

$$e_{Tr,i} = \frac{3}{2} \frac{R}{W_i} T \quad (2.6-7)$$

$$e_{Rot,i} = (n_i-1) \frac{R}{W_i} T \quad (2.6-8)$$

$$\begin{aligned} e_{vib,i} &= (n_i-1) \frac{R}{W_i} \left(\sum_v (E_{v,i}/k) \exp(-E_{v,i}/kT) \right) / Q_{vib,i} = e_{v,i}(T) \\ &= (n_i-1) \frac{R}{W_i} \theta_{v,i} / (\exp(\theta_{v,i}/T) - 1) \quad (2.6-9) \end{aligned}$$

for a SHO

$$e_{El,i} = \frac{R}{W_i} \left(\sum_{\ell} g_{\ell_i} (E_{\ell_i} / k) \exp(-E_{\ell_i} / kT) \right) / Q_{El,i} \quad (2.6-10)$$

The enthalpy per unit mass of a species i is,

$$h_i = e_i + \frac{R}{W_i} T + h_i^0 \quad (2.6-11)$$

where h_i^0 is the enthalpy of formation, per unit mass.

The specific heat of a species i at constant volume is

$$(C_v)_i = \left(\frac{\partial e_i}{\partial T} \right)_v = \sum_j (C_v)_{j,i} \quad (2.6-12)$$

The specific heat of a species i at constant pressure is

$$(C_p)_i = \left(\frac{\partial h_i}{\partial T} \right)_p = (C_v)_i + \frac{R}{W_i} \quad (2.6-13)$$

The pressure of a species i is

$$p_i = N_i kT \frac{\partial \ln Q_i}{\partial V} = \frac{N_i}{V} kT \quad (2.6-14)$$

A general reaction scheme can be represented by



where v_{ir} and v'_{ir} are the stoichiometric coefficients of the reactants and products of reaction r , respectively, and M_i is the chemical symbol of the species. The equilibrium constant for a reaction r is found from the law of mass action,

$$K_r(T) = \prod_i [M_i]_e^{\beta_{ir}} = \prod_i \left(\frac{Q_i}{N_{AV} V} \right)^{\beta_{ir}} \exp \left(-\sum_i \frac{W_i \beta_{ir} h_i^0}{RT} \right) \quad (2.6-16)$$

where subscript e denotes equilibrium, $\beta_{ir} = v'_{ir} - v_{ir}$ and N_{AV} is Avogadro's number.

For the solutions in the following sections either an equilibrium constant (using Equation 2.6-16 or a similar variant, with a SHO assumed), an equilibrium constant of the form

$$K_r(T) = C_r T^{-n_r} \exp(-\theta_d / T) \quad (2.6-17)$$

or an equilibrium constant deduced from "thermo-fit" data is used. In the thermo-fit method the enthalpy and free energy

are specified as a function of the translational temperature (Lordi et al. 1966 and Gordon and McBride 1971). This means that vibrational anharmonicity, vibration-rotation coupling and a more complicated electronic partition function can be included for high temperature reactions.

When the vibrational energy of species i is not in equilibrium, either frozen or relaxing, then $(C_v)_{vib,i}$ is zero and T in $e_{vib,i}$ is replaced by an effective vibrational temperature, T_v . T in the vibrational partition function is also changed to T_v for the nozzle solution (Lordi et al. 1966). In the normal shock solution of Garr and Marrone (1963) the equilibrium constant remains the same; instead of changing the vibrational partition function they allow the rate coefficient to be a function of vibrational energy. Clearly the thermo-fit method is not applicable when vibrational nonequilibrium occurs.

To examine the accuracy of the SHO which is commonly used for the vibrational energy of a diatomic molecule, the MO equilibrium vibrational energy of N_2 is plotted in Figure 2.16 against translational temperature. It can be seen that SHO is accurate at temperatures below 5000K and that the classical fully excited limit, RT/W_1 , is a good approximation at temperatures above 10000K.

2.6.2 Normal Shock

When studying relaxation rates behind a normal shock it is assumed that translation and rotation are always in equilibrium. Vibration may be in equilibrium for chemical relaxation studies but is sometimes not. The conditions behind the shock (subscript s) at which no relaxation has taken place (i.e. frozen conditions), can be found using these

assumptions, the state equation and the following three conservation equations for steady, adiabatic and quasi-one dimensional flow, if the initial conditions (subscript ∞) before the shock are known.

$$\text{Mass: } d\rho/\rho + du/u + dA/A = 0 \quad (2.6-18)$$

$$\text{Momentum: } dp + \rho u du = 0 \quad (2.6-19)$$

$$\text{Energy: } u du + dh = dh_o = 0 \quad (2.6-20)$$

where ρ is the density, u is the velocity, A is the cross-sectional area of a stream tube or nozzle, p is the pressure and h_o is the stagnation enthalpy. The state equation is found from Equation 2.6-14,

$$p = \sum_i p_i = k N_{AV} T \sum_i \frac{N_i}{V N_{AV}} = RT \sum_i \frac{\rho_i}{W_i} = \rho RT \sum_i c_i \quad (2.6-21)$$

where c_i is the number of moles of species i per gram of mixture. For a general gas, Vincenti and Kruger (1965) give the following iteration scheme for solving the shock jump relations for strong shocks. Using,

$$p_s = p_\infty + \rho_\infty u_\infty^2 (1-\epsilon) \quad (2.6-22)$$

$$h_s = h_\infty + \frac{1}{2} u_\infty^2 (1-\epsilon^2) \quad (2.6-23)$$

where $\epsilon \rho_s = \rho_\infty$, with $\epsilon = 0$ at first, a value of h_s can be found. Combining Equations 2.6-11 and 21 a relation

$$\rho = \rho(p, h) \quad (2.6-24)$$

can be found. This is used to find a corrected value of ϵ and the cycle is repeated with better values of ϵ . Similar methods are used by Garr and Marrone (1963) and Bittker and Scullin (1972). The final equilibrium conditions behind the shock could also be found in this way.

For the relaxing gas an additional equation is required. This is the rate equation of the form

$$Dc_i/Dt = \omega_i(p, \rho, c_j) \quad (2.6-25)$$

where $\{c_j\}$ is a finite set of relaxing parameters which may be energies of internal modes or species concentrations, as indicated here, (see Hayes and Probstein 1965 p.537). Thus the relaxing flow behind a normal shock is calculated by solving Equations 2.6-18, 19, 20, 25 and the general relation

$$h = h(p, \rho, c_i), \quad (2.6-26)$$

numerically.

The normal shock computer program (called NSHOCK for brevity) of Garr and Marrone (1963) and Garr, Marrone, Joss and Williams (1966), which uses a modified 4th order Runge-Kutta scheme (Treanor 1966), is used in Chapter 3. It can be used for vibrational and/or chemical relaxation with or without thermo-fit data. Its method of solution is similar to the brief description given here. The model of vibration-dissociation coupling that can be used is that of Treanor and Marrone (1962). For a multi-reaction, multi-species gas the linear rate law (Eq.2.4-4) is assumed and this may or may not lead to significant errors if rates found from various sources are used to predict overall rates for a hitherto unexamined system. Despite this, the linear rate law is assumed by NSHOCK for practical reasons.

Since the experimental work is restricted to mixtures of N_2 and N it is useful to use the atom mass fraction in the relevant equations. The atom mass fraction α is given by

$$\alpha = [N] W_N / \rho \quad (2.6-27)$$

with the molecular mass fraction given by

$$1-\alpha = [N_2] W_{N_2} / \rho. \quad (2.6-28)$$

Therefore the specific enthalpy and state equations become

$$h = \{(3.5+1.5\alpha)T + \alpha\theta_d\}R/W_{N_2} + (1-\alpha)e_v \quad (2.6-29)$$

where electronic energy is neglected, and

$$p = \rho RT(1+\alpha)/W_{N_2} \quad (2.6-30)$$

The generalised rate equation, for N_2 dissociation, becomes

$$D\alpha/Dt = \rho \{ k_d^{N_2} (1-\alpha) + 2k_d^N \alpha \} ((1-\alpha) - 4\rho\alpha^2/W_{N_2} K(T)) / W_{N_2} \quad (2.6-31)$$

The two possible rates are added together assuming a linear rate law. A similar relation is found for vibrational relaxation of N_2 and N mixtures with no dissociation,

$$De_v/Dt = (e_v(T) - e_v) / \tau_v \quad (2.6-32)$$

where $(1+\alpha)/\tau_v = (1-\alpha)/\tau_v^{N_2} + 2\alpha/\tau_v^N$.

2.6.3 Nozzle Flow

The nozzle flows to be examined in Chapter 3 are assumed to have been expanded from a reservoir of gas in chemical and vibrational equilibrium. Using this assumption, the three conservation equations 2.6-18, 19 and 20, the rate equation 2.6-25 and the relation 2.6-26, the nozzle solution is found. A is given as a function of distance along the nozzle. The equations are numerically integrated.

The reservoir or stagnation conditions are found by solving the shock jump relations for the equilibrium reflected shock conditions at the end of the shock tube, given the incident shock speed and initial pressure, and then assuming an isentropic expansion or compression of the gas to the measured stagnation pressure. These calculations are done with the computer program of McIntosh (1970) (called ESTC for brevity). This method is commonly used for reflected shock tunnels.

The nozzle flow computer program (called NENZF for brevity) of Lordi, Mates and Moselle (1966) is used in Chapter 3 for nonequilibrium expansions of N_2 and N mixtures with or without vibrational relaxation considered. The vibrational

de-excitation rate is used in a sudden freeze criterion which determines whether the vibrational energy is considered to be in equilibrium or frozen at some constant value. This assumption of uncoupled vibration-recombination seems justified on the basis of section 2.4.3.

The idea of "sudden freezing" of a relaxing variable such as α is due to Bray (1959). This has been examined for diatomic vibrational relaxation by Phinney (1963 and 1964). Following Bray (1970b), Equation 2.6-32 is rewritten as

$$-\frac{u de_v}{e_v dx} = \frac{1 - e_v(T)/e_v}{\tau_v} . \quad (2.6-33)$$

The left-hand side has the dimension of (time)⁻¹ and is at a maximum in the equilibrium limit; therefore a local flow time can be defined as

$$\tau_{fl} = - \left[\frac{u de_v}{e_v dx} \right]_e^{-1} \quad (2.6-34)$$

Combining 2.6-33 and 34,

$$\frac{\tau_v}{\tau_{fl}} \geq 1 - e_v(T)/e_v . \quad (2.6-35)$$

Using this relation it is seen that for near-equilibrium flow $\tau_{fl} \gg \tau_v$ and for near-frozen flow $\tau_{fl} \ll \tau_v$. If one wishes to assume vibrational equilibrium for part of the flow calculations and frozen vibration for the rest of the flow these inequalities are useful. A possible switchover point could be chosen at $\tau_{fl} = \tau_v$ or

$$\left| \frac{u de_v}{dx} \right|_e = \left(\frac{e_v}{\tau_v} \right)_e . \quad (2.6-36)$$

This criterion has been shown to be satisfactory by Phinney (1963). This sudden freeze criterion for vibrational relaxation is used for the nozzle flow calculations of pure N_2

and recombining N_2 and N mixtures. When the criterion first applies the frozen vibrational temperature T_v is made equal to the translational temperature. T_v is then used to calculate the frozen vibrational energy for the rest of the calculation. This method does not predict what final value T_{01} takes, only the value of $e_{v\infty}$.

2.6.4 Wedge Flow

By placing a flat wedge at sufficiently low incidence in the hypersonic nozzle flow an attached shock wave will be formed. If the temperature and density behind the shock are low enough it is possible to have a frozen flow over the wedge, i.e. the relaxation distance ($u\tau$) is very much greater than the wedge size. For this case the shock will be straight with an angle β , with respect to the free-stream. Given the wedge angle θ , β can be found using the following method.

The pressure and enthalpy equations 2.6-22 and 23 can be written as

$$p_s = p_\infty + \rho_\infty u_\infty^2 \sin^2 \beta (1 - \epsilon) \quad (2.6-37)$$

$$\text{and } h_s = h_\infty + \frac{1}{2} u_\infty^2 \sin^2 \beta (1 - \epsilon^2). \quad (2.6-38)$$

For vibrational equilibrium behind the shock at $T > 10000K$ and frozen chemistry the relation 2.6-24 can be explicitly stated as

$$\rho_s = (4.5 + 0.5\alpha_\infty) p_s / \{ (h_s - \alpha_\infty R \theta_d / W_{N_2}) (1 + \alpha_\infty) \} \quad (2.6-39)$$

for mixtures of N_2 and N . The free-stream enthalpy is

$$h_\infty = \{ (3.5 + 1.5\alpha_\infty) T_\infty + \alpha_\infty \theta_d \} R / W_{N_2} + (1 - \alpha_\infty) e_{v\infty}. \quad (2.6-40)$$

Thus p_s , ρ_s and h_s can be found for a given shock angle and free-stream by solving 2.6-37, 38, 39 and 40 iteratively, starting with $\epsilon = 0$. The corrected shock angle is found from the straight shock relation

$$\tan(\beta-\theta) = \epsilon \tan \beta \quad (2.6-41)$$

and thus,

$$\tan \beta = \epsilon^{-1/2} f(\eta_w) \quad (2.6-42)$$

where $f(\eta) = 2\eta / (1 + (1 - 4\eta)^{1/2})$ and $\eta_w = \epsilon^{1/2} \tan \theta / (1 - \epsilon)$ (see Hayes and Probstein 1965 p.218). The new value for β is used in the iteration procedure until ϵ and β converge to their correct values. Thus a shock angle on the flat wedge is determined by the free-stream conditions and the wedge angle, so it could be used, in principle, to determine $e_{v\infty}$ and α_∞ .

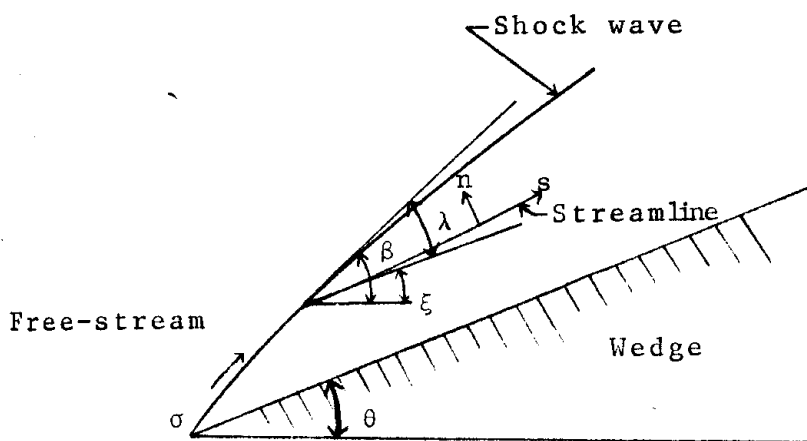
2.6.4.1 Shock Curvature

If the relaxation distance is comparable to the wedge size, the relaxation effects can be observed. The pressure and flow velocity are only relatively slightly affected by the relaxation process, so that the strong decrease in translational temperature associated with the redistribution of energy in the relaxing mode is accompanied by a strong rise in density. Through Equation 2.6-41 it is seen that the density rise will cause the shock angle to decrease. It can be shown that the initial shock curvature at the tip is directly proportional to the relaxation rate at the tip. A brief derivation is given here.

Using natural coordinates s and n , where s is the distance along a streamline and n the distance along the normal to the streamline, the following equation can be obtained from the appropriate mass, momentum and energy conservation equations, the state equation and the general rate equation (see Vincenti and Kruger 1965 p.301 and Sedney 1970 p.176):

$$\frac{(M_f^2 - 1)}{\rho u^2} \frac{\partial p}{\partial s} + \frac{\partial \xi}{\partial n} + \frac{j \sin \xi}{y^r} = \frac{\Sigma h_c i \omega_i}{\rho u h_\rho} \quad (2.6-43)$$

where M_f is the frozen Mach number u/a_f , where $a_f = [(\partial p/\partial \rho)_{S, c_j}]^{1/2}$ is the frozen speed of sound (S being the specific entropy), ξ is the streamline inclination behind the shock, $j = 0$ for a wedge, $= 1$ for a cone, y' is the coordinate perpendicular to the axis of symmetry, and $h = h(p, \rho, c_j)$ is the specific enthalpy and so $h_{c_i} = (\partial h/\partial c_i)_{p, \rho, c_j} (i \neq j)$, $h_\rho = (\partial h/\partial \rho)_{p, c_j}$.



From the geometry of the above figure,

$$\frac{\partial}{\partial \sigma} = \cos \lambda \frac{\partial}{\partial s} + \sin \lambda \frac{\partial}{\partial n} = \frac{\partial \beta}{\partial \sigma} \frac{\partial}{\partial \beta} \quad (2.6-44)$$

where $\lambda = \beta - \xi$ and $\frac{\partial \beta}{\partial \sigma}$ is the shock curvature κ . Using this equation and 2.6-43 an expression for $\partial p/\partial s$ can be found. An alternative expression for $\partial p/\partial s$ is given by the ^{equation} n -momentum λ and 2.6-44. Equating these two expressions, κ is found to be (see Sedney 1961, Capiiaux and Washington 1963 and Becker 1972) given by

$$\kappa = \left\{ \frac{\sum h_{c_i} \omega_i}{\rho u h_\rho} - \frac{j \sin \xi}{y'} - \frac{\partial \xi}{\partial s} (\tan \lambda (M_f^2 - 1) - \cot \lambda) \right\} / \left(\frac{\partial \xi}{\partial \beta} / \sin \lambda + (M_f^2 - 1) \frac{\partial p}{\partial \beta} / \rho u^2 \cos \lambda \right) \quad (2.6-45)$$

For the initial shock curvature at the tip of a wedge, ξ is the wedge angle, $j = 0$ and $\partial \xi/\partial s$ is the wedge curvature ($= 0$)

for a flat wedge). The derivatives $\partial\xi/\partial\beta$ and $\partial p/\partial\beta$ are given by Kewley (1974).

To calculate the variation of shock curvature along the shock it is required that the variation of ξ along the shock is known. One method of finding this variation is to use the nonequilibrium method of characteristics given by Sedney (1970). Using this reference extensively, a computer program (called NMOCW for brevity) to solve for flat or curved wedges is given by Kewley (1974). This is used to calculate both the shock curvature variation with shock angle and the complete flow field for the wedge flows in Chapter 3. Relaxation rate models of the type given in this section 2.6 are used.

2.7 Summary

In this chapter, the conventional vibrational and chemical relaxation rate models for diatomic gases, specifically H_2 and N_2 , have been examined by comparing them with results of a detailed microscopic description of the relevant processes. Using the vibrational Master equation, four of the theoretical questions posed in the Introduction have been studied and the results summarised in section 2.5. A brief description of the methods of solution to be used to examine the experimental results of Chapter 3 has been given for normal shocks, nozzle expansions and flow over a wedge. The relaxation rate models, used in these solutions, are of the conventional type because the more complex model presented in this chapter is not practical, due to the large computing times required for any diatomic gas, other than H_2 . However the limitations shown in this chapter, of the conventional relaxation rate models, are now recognized.