

1.1 Aim

If a gas in thermodynamic equilibrium undergoes a sudden change in a state variable then it will take a finite time, say τ , to equilibrate. The speed at which the gas tends toward equilibrium is called the relaxation rate (v_l/τ). A convenient state variable is the pressure, which can be increased, by a shock wave, or decreased, by a supersonic nozzle expansion, fast enough for nonequilibrium to occur. The aim of this thesis is to study the relaxation rates of gases with diatomic molecules theoretically and experimentally behind shock waves and along nozzles. A feature of this work is the examination of relaxation rates behind a shock wave in a nozzle-produced nonequilibrium flow.

At sufficiently high temperatures a gas of diatomic molecules and atoms, out of equilibrium, will undergo vibrational relaxation and/or chemical reaction. Since these processes occur as a result of molecular collisions it follows that the rates will increase with temperature and density. Usually these rates have different speeds so that they may be studied separately. However, as the temperature increases, the vibrational and chemical relaxation rates converge. Some attention is therefore given to this aspect here. It is assumed that the translational and rotational energy are in equilibrium while the energy of electronic excitation is either in equilibrium or neglected. Ionization of the molecules is included, when necessary, in the analysis of the experiments.

The vibrational relaxation and chemical reaction rates of nitrogen are investigated using the free-piston shock

tube DDT and the free-piston shock tunnels T2 and T3 at the Australian National University in the Department of Physics. By placing a model in the nonequilibrium hypersonic expansion generated by a shock tunnel, relaxation rates behind a shock in a nonequilibrium flow are studied.

A justification for, and more details on, research presented in this thesis are given in the Historical Review and Planned Research sections of the Introduction.

1.2 Historical Review

Considerable research, both theoretical and experimental, has been carried out in the field of nonequilibrium gas dynamics and a number of comprehensive books have been published (see Bradley 1962, Gaydon and Hurle 1963, Clarke and McChesney 1964, Vincenti and Kruger 1965, Zel'dovich and Raizer 1966 and Stupochenko, Losev and Osipov 1967). Three more recent reviews have been made by Belford and Strehlow (1969), Rich and Treanor (1970) and Bray (1970b). These references provide an extensive survey of the general field up to 1970.

However since 1970 the field is still continuing, particularly in supersonic gas flow laser research, and so the review here does not claim to be comprehensive; even though a third of this thesis' references appeared during the last three years. The review aims to point out some interesting unexamined theoretical questions and previously unobtainable experimental results that could lead to further insight into the mechanisms of diatomic relaxation rates.

1.2.1 Vibrational Relaxation

For a vibrationally relaxing diatomic gas, Landau and Teller (1936) showed that the relaxation rate can be

represented by:

$$\frac{de_v}{dt} = \frac{e_v(T) - e_v}{\tau_v} \quad (1.2-1)$$

where e_v is the vibrational energy per unit mass of gas, $e_v(T)$ is the equilibrium value of e_v at T and τ_v is the vibrational relaxation time, which is a function of pressure and temperature. This is the simplest form of relaxation rate and can also be applied to near-equilibrium chemical relaxation (Vincenti and Kruger (1965) p.242). This equation was first used in the acoustic problem of sound dispersion in gases. It was first used for studying vibrational relaxation behind shock waves by Bethe and Teller (1941), which is why the equation is sometimes called the Landau-Teller or Bethe-Teller equation. In deriving the equation it was assumed that the diatomic molecule is a harmonic oscillator (HO). This implies that:-

(1) the vibrational energy transitions are limited to steps of one vibrational level only i.e. one-quantum transitions;

(2) the vibrational transition rates between the levels vary linearly with level number;

(3) the vibrational energy levels are equally spaced, and

(4) the populations of the vibrational levels can be described by a Boltzmann distribution in terms of a vibrational temperature T_v , i.e. $e_v = e_v(T_v)$ given by:-

$$e_v(T_v) = \frac{(R/W)\theta_v}{\exp(\theta_v/T_v)-1} \quad (1.2-2)$$

where θ_v is the characteristic vibrational temperature

of the molecule, W is its molecular weight and R is the universal gas constant.

To study high temperature ($T > 1000\text{K}$) vibrational excitation rates, normal shock waves produced in conventional shock tubes are commonly used (see Stupochenko et al. (1967) for a review of techniques). Measurements of τ_v have generally shown the validity of Eq. 1.2-1 for different gases (Millikan and White (1963b), Kiefer and Lutz (1966) and Lutz and Kiefer (1966)). However there are a number of experiments which show that Eq. 1.2-1 is not universally applicable. Appleton (1967) showed that for pure N_2 , at temperatures above 5500K, τ_v appears to be dependent on the amount of vibrational excitation. This means that as equilibrium is approached, and thus the temperature decreases, τ_v decreases. Further experiments by Hanson and Baganoff (1970) and Hanson (1971) for N_2 and CO also show this effect, using another experimental technique. Simpson (1973), on the other hand, suggests that the effect is not real. An explanation of this possible effect will require a more detailed model of the vibrational relaxation rate.

The Landau-Teller vibrational rate equation implies that for de-excitation the value of τ_v is the same as that for excitation. Hurle, Russo and Hall (1964) using a shock tube with a hypersonic nozzle at the end, i.e. a shock tunnel, measured the "vibrational temperature", T_v , of pure N_2 using the sodium-line reversal technique (SLR). Assuming the N_2 to be in a Boltzmann equilibrium at T_v , they showed that τ_v was smaller than the value obtained from normal shock experiments using the same technique (Hurle 1964). Experiments since then in N_2 , CO and O_2

are described in Rich and Treanor (1970) and Hurle (1971), where $\phi = \tau_v(\text{SHOCK})/\tau_v(\text{NOZZLE})$ varied from 70 to 5 for N_2 , 5 to 1 for CO and was 0.1 for O_2 . This apparent discrepancy of the relaxation rates measured in shock waves and expansion flows has led to a reappraisal of the Landau-Teller theory.

Bray (1968) and Treanor, Rich and Rehm (1968) have shown that the vibrational relaxation of a system of anharmonic oscillator molecules, including vibration to vibrational energy exchange between the molecules (V-V), under isothermal conditions can give rise to a non-Boltzmann distribution of vibrational energy which leads to faster relaxation rates, when the vibrational energy is high and the translational temperature is low. Bray (1970a) also found that rapid changes in the translational temperature can lead to increased relaxation rates. However experimental comparison with theory (Blom, Bray and Pratt 1970), though predicting the right trend, lacks quantitative agreement. Very dilute (0.5%) CO in Ar experiments, in an unsteady expansion, by McLaren and Appleton (1970) gave a value of ϕ equal to one. This meant that the absence of V-V effects correlated with the Landau-Teller model.

The impetus of supersonic gas flow laser research has led to the development of the CO- N_2 (McKenzie 1972, first reported in 1970) and the CO-Ar (Watt 1971) gas dynamic lasers. Center and Caledonia (1971), Caledonia and Center (1971) and McKenzie (1972) have done numerical calculations of these laser flows using the same type of model as Bray and Treanor et al. and have shown that they can predict the

features of the flows. Direct comparisons have yet to be made because of the uncertainties in the parameters in their laser models. However Center and Caledonia (1972) have compared detailed numerical results with the experiments of von Rosenberg, Taylor and Teare (1968 and 1971) in CO and CO-Ar and with Teare, Taylor and von Rosenberg (1970) in CO-N₂. They concluded that ϕ for CO was less than or equal to five, that the vibrational energy relaxation rate cannot be increased by more than a factor of 2 by anharmonic effects and that the "vibrational temperature" relaxation rate is not the same as the vibrational energy relaxation rate. They also found that ϕ for N₂ cannot be as large as 70, in agreement with Teare et al. (1970) and experiments by Watt and Rich (1971) in CO-N₂. Cleaver and Crow (1973), for an unsteady expansion of pure O₂, have shown that $\phi \approx 1$. In summary it appears that more recent work, not using the SLR technique, in N₂, CO and O₂ has shown that ϕ is less than five. It should be pointed out that static pressure measurements for a pure N₂ nozzle expansion by Nagamatsu and Sheer (1965) gave $\phi \approx 1$.

Since the N₂ vibrational energy and "temperature" relaxation rates are being used in supersonic gas flow laser analyses for CO-N₂ and CO₂-N₂ (Daffey 1973 and Lee 1974), a large value of ϕ for N₂ would lower the overall efficiency and operating range of such systems. The SLR technique has been reinterpreted by MacDonald (1972), for N₂-Ar expansions, who showed that the old interpretation (Hurle et al. 1964 and Hurle 1964) gave ϕ ranging from 20 to 3000 while his interpretation gave $\phi \approx 1$. This is expected in diluted N₂ because there would be insufficient

N_2 - N_2 collisions for V-V effects to occur. Detailed comparisons between theory and experiment for pure N_2 (Hurle et al. 1964) had not been made to see whether ϕ was indeed less than five. Further experiments in pure N_2 using another technique would be useful.

Since flows of N_2 and N mixtures are studied in this thesis it is important to consider the effect of vibrational relaxation of N_2 by collisions with N. Bauer and Tsang (1963) have proposed various mechanisms for vibrational relaxation which had faster relaxation rates than vibration to translation energy exchange (V-T) by inelastic collisions. They predicted that N and O atoms would increase the relaxation rate by atom exchange reactions such as $N'N' + N'' \rightarrow N' + N'N''$. This mechanism was faster than the extrapolated usual rates of temperatures above 4000K for oxygen and 6000K for nitrogen.

Kiefer and Lutz (1967) and Breen, Quy and Glass (1973a) have shown that the O_2 self atom vibrational relaxation rate was 2-3 orders of magnitude faster than that for pure O_2 for a temperature range 1000-3400K. Breshears and Bird (1968) showed that the vibrational relaxation rate of N_2 by O was nearly two orders of magnitude faster than that for pure N_2 for a temperature range of 3000-4500K. The vibrational relaxation rate of CO by O was found by Center (1973) to be 2-3 orders of magnitude larger than that for pure CO for a temperature range 1800-4000K. Relaxation of CO by H atoms is also very fast compared to pure CO (von Rosenberg et al. 1971). These results have been attributed to a "chemical" effect by these workers

because of the stability of O_3 , N_2O and CO_2 (see also Nikitin and Umanski 1972). If this is the case then the N_2 by N vibrational relaxation rate should not be greatly different than that for pure N_2 as N_3 is unstable. Some evidence for this suggestion could be the null result of Breen, Quay and Glass (1973b) for H_2 by H vibrational relaxation.

In summary, even though the Landau-Teller equation is often adequate for vibrational relaxation, a more detailed theory is needed to explain all the anomalies. Some further experimental work in undiluted N_2 is suggested.

1.2.2 Chemical Relaxation

For the dissociation and recombination of a pure diatomic gas, such as N_2 ,



then

$$-d[N_2]/dt = k_d[N_2][M] - k_r[N]^2[M] \quad (1.2-4)$$

where k_d and k_r are the dissociation and recombination rate coefficients, respectively. The symbol M refers to N_2 or N. In chemical equilibrium the rate coefficients are related to each other by the rate-quotient law,

$$k_d/k_r = K(T) \quad (1.2-5)$$

where $K(T)$ is the equilibrium constant at T. The validity of this equation during a reaction has been subject to considerable analysis (Keck and Carrier 1965, Bray and Pratt 1967, McElwain and Pritchard 1970 and 1971, Shui, Appleton

and Keck 1970 and Labib, McElwain and Pritchard 1972). It has been shown that behind a shock, after an initial transient period (commonly called the induction time), Eq. 1.2-5 holds. For a nozzle flow it may only be approximate (Bray and Pratt 1967). However all this work did not include V-V effects which had been found by Bray (1968 and 1970a) and Treanor et al. (1968) to have an effect on the vibrational relaxation rate, especially in an expansion.

Usually dissociation occurs after vibrational equilibrium has been reached and most shock tube determinations of k_d for diatomic molecules have been made using this assumption (see Stupochenko et al. 1967). Most readily obtainable, stable, diatomic molecules have been studied in a shock tube (Belford and Strehlow 1969). The dissociation rate coefficients are conventionally given by

$$k_d = CT^{-n} \exp(-\theta_d/T) \quad (1.2-6)$$

where C and n are experimentally found constants and θ_d is the characteristic dissociation temperature of the molecule. The value of n is given in a classical theory by Vincenti and Kruger (1965 p.221). It assumes that the vibrational, rotational and translational modes are in equilibrium and that the only collisions causing dissociation are those for which the net energy of collisions is greater than the molecular binding energy. Thus n varies from 0.5 to 1.5. Shock tube measurements of O_2 , N_2 , CO and NO in inert heat baths have led to values in agreement with these limits (see Stupochenko et al. 1967 p.328). However for pure O_2 experiments the rate coefficient for O_2-O_2

collisions had a value of 2.5.

Recently Hanson and Baganoff (1972) measured the rate coefficients for N_2-N_2 and N_2-N collisions in pure N_2 and gave the values of 4.5 ± 1 and 2.5 ± 1 respectively. They used a reflected shock pressure measurement technique. It would be of interest to confirm this result using another technique.

To measure the dissociation rate coefficients of N_2 by N_2 ($k_d^{N_2}$) and N_2 by N (k_d^N) it is necessary to assume the linear rate law:-

$$k_d = (k_d^{N_2}[N_2] + k_d^N[N])/([N_2] + [N]). \quad (1.2-7)$$

Kiefer (1972) has shown that this equation can fail for H_2 and H in Ar and has interpreted the results of Hurle, Jones and Rosenfeld (1969) as evidence. Breshears, Bird and Kiefer (1971) and Breshears and Bird (1973a) appear to have demonstrated its applicability for O_2 in inert gas and H_2 and H in Ar and Xe for a diatomic gas concentration of up to 20%. Dissociation rate measurements in a free stream of N_2 and N could provide a test of Eq. 1.2-7.

As mentioned already, most shock tube experiments assumed vibration to be in equilibrium before dissociation occurred but this is not always true. The existence of induction times, the time (measured from the shock arrival) before steady dissociation occurs, has been shown for O_2 (Wray 1962, Watt and Myerson 1969 and Breshears, Bird and Kiefer 1971), HCl (Breshears and Bird 1972), H_2 (Breshears and Bird 1973a) and F_2 (Breshears and Bird 1973b). Incubation time was the previous name used by Wray (1962) for this phenomenon. Usually the relaxation region behind

the shock can be divided into three parts: the vibrational relaxation zone, an induction distance with vibration in "quasiequilibrium" and the chemical relaxation zone.

However induction times less than τ_v occur for O_2 -Ar dissociation (Wray 1962) at temperatures above 10000K implying that here dissociation occurs before vibrational "quasiequilibrium" is established. Thus vibration and dissociation must be coupled in the high temperature limit.

Theoretical models for induction times caused by vibration-dissociation coupling have been given by Treanor and Marrone (1962), Marrone and Treanor (1963), Brau, Keck and Carrier (1966), Dove and Jones (1971) and Wengle (1973) but V-V effects were not considered.

An induction time for N_2 has been observed by Hornung (1972) behind the bow shock of a cylinder in a shock tunnel. This was found to fit an expression suggested by Shui, Appleton and Keck (1970) on the basis of a model which depended on the excitation of an electronic state. It would be of interest to observe an induction time in a shock tube as this might confirm whether the phenomenon is caused by vibration-dissociation coupling or by an electronic excitation effect. An induction time for CO has also been found, which was consistent with the presence of C_2 or an electronic state of CO as an active intermediate species, by Appleton, Steinberg and Liquornik (1970). Experiments by Hanson (1973) have indicated that C_2 is the more likely intermediate species.

Experimental recombination of diatomic molecules along a hypersonic nozzle expansion has been studied by Nagamatsu

and Sheer (1965) for N_2 and air, Duffy (1965) for air, Russo, Hall and Lordi (1966) for H_2 -Ar and Zonars (1967) for air using static pressure measurements. However more accurate estimates of recombination rates need a more sensitive diagnostic technique (Bray 1970b). An attempt was made by Stalker and McIntosh (1973) to measure the atom mass fractions of oxygen and nitrogen in a hypersonic nozzle expansion of air. They showed that a shock angle on a wedge could be used to determine the ratio of monatomics to diatomics in the free stream. The effect of He contamination cannot be distinguished until late in the flow and this could invalidate their high enthalpy results. Mass spectrometer results for N_2 recombination in T3 just completed by Crane (1975) show that He contamination can be significant and the atom mass fraction is lower than expected at high stagnation enthalpies (> 30 MJ/kg).

Theoretical calculations of recombining flows are usually made with recombination rates deduced from shock tube experiments using Eq. 1.2-5 (Lordi, Mates and Moselle 1966 and Bittker and Scullin 1972). Bray and Pratt (1967), Tirumalesa (1967) and Labib, McElwain and Pritchard (1972) have examined coupled vibration-recombination but did not include V-V effects. These three references illustrate the uncertainties in the theories. For instance Bray and Pratt found that τ_v would be larger in some cases ie $\phi < 1$, Labib et al. found $\phi = 1$ and Tirumalesa had $\phi > 1$. It should be pointed out that each used different nozzle flows. Experimental measurements of ϕ in recombining flows could remove the uncertainties. By using undiluted gases the

importance of V-V effects could be found.

In summary, it appears that while the features of dissociation behind shock waves are well known, the study of recombination along a hypersonic nozzle still needs further experiments and theoretical work. Experiments in undiluted N_2 could provide insight into both relaxation processes.

1.3 Planned Research

In the preceding section a review has been made of the past work on relaxation rates of gases with diatomic molecules at temperatures where vibrational and/or chemical relaxation is important. In this section details of the theoretical and experimental program will be given. It aims to complement the previous work in this field and is based on suggestions in the last section. All experiments are made in pure N_2 .

The major facilities used (for the work presented in this thesis) are the Australian National University, Computer Centre, Univac 1108 and PDP 11-45 and the Department of Physics free-piston shock tube DDT and free-piston shock tunnels T2 and T3. The features of these facilities are:-

1. The Univac 1108 is a time-sharing computer with interactive terminals providing for rapid development and short program running times (the typical maximum run time used is about 5 minutes). Plotting is done via the PDP 11-45.

2. The free-piston technique, developed to its present state by Dr R.J. Stalker (see Stalker 1966, 1967, 1972 and 1974), is ideal for very flexible, quick and

inexpensive experiments. Experiments at pressures and temperatures, hitherto inaccessible (Hornung 1971), can be routinely carried out in N_2 .

The free-piston shock tunnel is a shock tube with a hypersonic nozzle (usually conical) attached to the end. The shock tube consists of a tube containing the test gas separated by a strong diaphragm from the driver section. The driver section in the free-piston shock tube contains a free piston which is projected along the tube by a reservoir of moderately high pressure air. In front of the piston the driver gas, usually helium, is compressed adiabatically to very high pressure and temperature. The diaphragm ruptures and a shock wave is created in the test gas which is reflected back from the end of the tube. This creates a high enthalpy reservoir for the flow through the nozzle once a thin diaphragm at the nozzle entrance is ruptured. A model placed in the hypersonic nozzle flow will have a standing shock on or in front of it.

Figure 1.1 shows a schematic shock tunnel. The study of relaxation rates can be made in three places; in principle the studies could be made simultaneously. Relaxation, after a pressure and temperature increase, can be studied behind a shock wave with an equilibrium or nonequilibrium test gas. Relaxation, in response to a decrease in the pressure and temperature, can be studied in the nozzle expansion from an equilibrium test gas.

1.3.1 Vibrational Relaxation

The theoretical aspects to be examined are:-

1. Does the vibrational excitation rate increase as equilibrium is approached, as may have been observed by Appleton (1967), Hanson and Baganoff (1970) and Hanson (1971)?

2. What is the value of ϕ for the pure N_2 nozzle expansions of Hurle et al. (1964)?

Both 1. and 2. are to be examined considering the theories of Bray (1968 and 1970a) and Treanor et al. (1968), successfully used by Center and Caledonia (1972) for CO expansions.

The experimental projects to be done are:-

3. Attempt to measure ϕ for pure N_2 nozzle expansions in the small shock tunnel T2 over a range of reservoir temperatures of 3000-9000K. This is to be done using straight shock angles on wedges in the free stream to measure $e_{v\infty}$.

4. Attempt to measure τ_v behind an oblique shock in the nozzle of T2 for N_2 by N_2 -and N_2 by N relaxation, using optical interferometry and the shock curvature technique.

1.3.2 Chemical Relaxation

The theoretical aspects to be examined are:-

1. Vibration-dissociation coupling behind shock waves including V-V effects, shown to be important for vibrational relaxation. This includes induction times and the linear rate law.

2. Vibration-recombination coupling along nozzles including V-V effects. Does the rate-quotient law (Eq. 1.2-5) apply in a nozzle?

3. Attempt to explain just completed mass spectrometer measurements (Crane 1975) of the atom mass fraction of N_2 in the nozzle expansion of the large shock tunnel T3.

The experimental projects to be done are:-

4. Verify the strong temperature dependence of the pre-exponential factor of the undiluted N_2 dissociation rates reported by Hanson and Baganoff (1972). This is to be done in the shock tube DDT using time-resolved optical interferometry.

5. Attempt to measure the dissociation rates of N_2 by N_2 and N_2 by N behind an oblique shock in the nozzle flow of T3 using optical interferometry and the shock curvature technique. The reservoir temperature range is 9000-11000K.

1.4 Outline of Thesis

The Introduction gives the aim, a historical review of past work and details of the research program to be carried out in this thesis. Both theory and experiment are related to studying diatomic relaxation rates, of N_2 in particular, in a shock tunnel. Vibrational and chemical relaxation are to be investigated.

In Chapter 2, the theoretical work is presented. A "ladder climbing" model of diatomic relaxation is developed and applied to both vibrational and chemical relaxation. A first-moment solution of the Master equation is examined first and then a full solution is given. The conclusions of this model are used to determine the applicability of conventional phenomenological relaxation rate solutions.

These solutions are used later to investigate experimental studies of relaxation behind a normal shock, along a nozzle and over a wedge.

In Chapter 3, the experimental work is presented. The dissociation rates of N_2 , behind a normal shock wave, are measured in the free-piston shock tube DDT. Using the small free-piston shock tunnel T2, the vibrational de-excitation rate of N_2 along a hypersonic nozzle is measured. By placing a flat plate in the flow, at sufficient incidence, the excitation rate of N_2 by N_2 and N_2 by N is investigated behind the oblique shock. In the large free-piston shock tunnel T3 the experimental measurements, in N_2 , of the atom mass fraction and He contamination are examined. Dissociative relaxation over a wedge is investigated.

The conclusions of the thesis are presented in Chapter 4, along with suggestions for future work.