4. CONCLUSIONS

4.1 Thesis Results

In this thesis, the vibrational and chemical relaxation rates of diatomic gases have been investigated both theoretically and experimentally. The Historical Review (section 1.2) was used as a basis for the research presented here, which was primarily to study flow behind a shock in a nonequilibrium free-stream. However, before the analysis of experiments was made, it was necessary to examine the conventional models of vibrational and chemical relaxation rates in more detail to determine whether they could be used in the analysis.

The diatomic molecules are represented by the anharmonic Morse Oscillator. The vibrational Master equation was constructed by allowing one-quantum vibration to translation (V-T) energy exchanges and vibration to vibration (V-V) energy exchanges between the molecules. Dissociation was allowed to occur from the uppermost vibrational level. With this detailed microscopic model of the diatomic relaxation processes, the theoretical questions posed in section 1.3 were examined, for H_2 and N_2 specifically, and the results are summarised in section 2.5. The most important result was that it appears valid, for the cases examined, to use conventional nozzle flow programs, with shock-tube-determined dissociation and vibrational excitation rates, to calculate recombining and vibrationally de-excitating flow. The effect of V-V transitions on lowering T_{01} for vibrational de-excitation in the nozzle flow confirms previous work (Bray 1968 and 1970a). An interesting result which needs experimental confirmation was that T_{01} increases above

the value predicted without V-V transitions in a recombining flow. The theoretical work shows that the conventional models of relaxation rates are suitable for analysing experiments provided that their limitations are recognised; for example, the linear rate law for dissociation could be incorrect.

The experimental studies, listed in section 1.3, were restricted to vibrational and chemical relaxation of undiluted nitrogen. An advantage of nitrogen over carbon monoxide as a gas to be studied is that the extreme sensitivity of CO to impurities is not expected in N_2 (Hurle 1971). However, a disadvantage is that N_2 is not readily accessible to direct spectroscopic studies; usually additions of Na, Cr or CO are required. The present method of studying nitrogen relaxation was to observe the flow by means of a Mach-Zehnder interferometer. The dissociation rates of undiluted nitrogen were measured in the free-piston shock tube DDT, using time-resolved optical interferometry, and confirmed the strong temperature dependence of the pre-exponential factor observed by Hanson and Baganoff (1972). The reason for this unusually strong temperature dependence was anticipated to be due to V-V effects (see Kiefer 1972); however, this was not observed in the results of theoretical calculations for H_2 dissociation. An extensive set of theoretical calculations for N_2 could not be made because of the long computation times that would have been necessary. The vibrational de-excitation and excitation rates of nitrogen were measured in the free-piston shock tunnel T2 by measuring the shock angles and curvatures, from optical interferograms, of flow over an inclined flat plate in the nonequilibrium

nozzle flow. The de-excitation rate was within a factor of ten of the shock-tube-determined excitation value. The excitation rate of N_2 by collision with N was measured to be less than about 50 times the excitation rate of N_2 by N_2. Experiments with dissociating nitrogen flow over a wedge, in the partially dissociated nitrogen nozzle flow of the shock tunnel T3, were examined. The initial shock curvature, measured from optical interferograms was used to deduce the initial dissociation rate. The measured relative species concentrations of N_2, N and He contamination, found by Crane (1975) with a mass-spectrometer, are used to calculate the free-stream for the wedge flows. The experimental results for initial shock curvature fall between the theoretical values, calculated with accepted rates for nitrogen dissociation, when helium contamination is included for the higher enthalpy experiments.

It was shown that many of the relaxation effects observed with diatomic molecules could be explained by the results of detailed study of the Master equation including V-V effects, and that suitable techniques, involving measurements of flow parameters only, can be devised to measure the various relaxation rates of interest in free-piston facilities.

4.2 Suggestions for Further Related Research

The theoretical model of diatomic relaxation rates developed here could be improved by including multi-quantum transitions, rotation effects and dissociation from other vibrational levels. A major improvement can be made once a definite set of *a priori* transition probabilities is generally agreed upon. The problem of computer time can probably only be resolved by waiting until faster computers become available.

On the experimental side, a number of further experiments could be undertaken. The induction time for nitrogen observed by Hornung (1972a) was not resolvable in the shock tube experiments. To decide whether this phenomenon is an electronic effect (Shui, Appleton and Keck 1970) or the result of vibration-dissociation coupling (as for O_2, see Wray 1962) it will be necessary to do further experiments, possibly using the laser schlieren technique of Breshears, Bird and Kiefer (1971), at lower densities. Also, the free-stream conditions used by Hornung (1972a), to correlate the induction time, need to be recalculated with He contamination. This was not done in the thesis because of insufficient time. Some experiments in N_2-He mixtures on flow over a circular cylinder, by Pratt and Kewley (1974), also appear to show this induction time. Thus the investigation of the induction time for N_2 dissociation provides a number of possible experiments.

The method of calculation for the helium contaminated flows in T3 depended critically on knowing the free-stream velocity accurately. Measurements of this velocity for the same nozzle flows as in Crane (1975) are very necessary if quantitative comparisons between theoretical and experimental α's are to be made.

As a test of the Master equation results in Chapter 2, measurements of T_{01} in recombining nitrogen flows would be valuable. Experiments of this type were contemplated for this thesis but again lack of time was the deciding factor. The temperature of T_{01} is anticipated to be too high (see Table 3.2) for the SLR method but the brightness-emissivity method of Parkinson and Reeves (1964) could be attempted. For recombining carbon monoxide flows, the CO laser absorption method of Chackerian and Weisbach (1973) could also

be tried.

The problems caused by the divergence effect of the conical nozzle flows can be removed once contoured nozzles are made for the relevant flows. The method of characteristics program of Kewley (1974) can easily be converted to calculate nonequilibrium two-dimensional or axisymmetric nozzle flows. At the present time, some frozen flow calculations by Mr M.D. Daffey, in conjunction with NENZF, have proved successful in designs for a contoured nozzle.