VIBRATION AND CHEMICAL RELAXATION RATES OF DIATOMIC GASES

by

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To my wife Anita

and daughter Lisa
The contents of this thesis, except as described in the Acknowledgements and where credit is indicated by reference, are entirely my own work.

(Douglas John Kewley)
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ABSTRACT

A theoretical and experimental study of the vibrational and chemical relaxation rates of diatomic gases, in flows behind shock waves and along nozzles, is made here.

The validity of the conventional relaxation rate models, which are generally used to analyse experiments, is tested by developing a detailed microscopic description of the diatomic relaxation processes. Assuming the diatomic molecules to be represented by the anharmonic Morse Oscillator, the vibrational Master equation, which describes the time variation of each vibrational energy level population, is constructed by allowing one-quantum vibration to translation (V-T) energy exchanges and vibration to vibration (V-V) energy exchanges between the molecules. Dissociation and recombination are allowed to occur from, and to, the uppermost vibrational level. Solving the Master equation, it is found that a number of effects are explained by the inclusion of V-V transitions. In particular, it is found that V-V energy exchanges cause the induction time for H₂ dissociation to be increased; suggest that the linear rate law, for H₂ and Ar mixtures, fails for a H₂ mole fraction above 20%; give an acceleration of vibrational excitation as equilibrium is approached for H₂ and N₂; cause the vibrational temperature to be lower than the value found without V-V transitions for vibrational de-excitation in nozzle flows of H₂ and N₂, and conversely for recombination of H₂ in nozzle flows. The most important result is the demonstration that conventional nozzle flow calculations, with shock-tube-determined dissociation and vibrational excitation rates, appear to be valid.
for the recombining and vibrationally de-excitating flows considered.

The dissociation rates of undiluted nitrogen are measured in the free-piston shock tube DDT, using time-resolved optical interferometry, over a temperature range of 6000-14000K and confirm the strong temperature dependence of the pre-exponential factor observed by Hanson and Baganoff (1972).

The vibrational de-excitation and excitation rates are determined in the small free-piston shock tunnel T2 over temperature ranges of 2000-4000K and 7000-10300K, respectively, 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 is found to be within a factor of ten of the excitation rate, while the excitation rate of $N_2$ by collision with $N$ is found to be less than about 50 times the excitation rate of $N_2$ by $N_2$. The dissociation rates of nitrogen, in the flow behind a shock attached to a wedge, are investigated in the large free-piston shock tunnel, using the shock curvature technique. The discrepancy, reported by Kewley and Hornung (1974b), between theory and experiment at the highest enthalpy is found to be resolved by including the measured helium contamination (Crane 1975) in the free-stream. Reasonable agreement is obtained between experimental shock curvatures and calculations using accepted dissociation rates.
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