

VIBRATIONAL AND CHEMICAL RELAXATION
RATES OF DIATOMIC GASES

by

Douglas John Kewley

A thesis submitted for the
degree of Doctor of Philosophy
at the Australian National University

Canberra

April 1975

*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)

ACKNOWLEDGEMENTS

I wish to sincerely thank my supervisor Dr H.G. Hornung for his advice and general assistance during my course of study. I also wish to thank Dr R.J. Stalker for being my supervisor during Dr Hornung's study leave and for his continued advice and co-operation.

I would also like to thank the following people for their assistance towards the preparation of this thesis: Dr R.J. Sandeman for his help with the interferometer; Mr R. French for his excellent contributions and technical knowledge relating to the free-piston facilities; Mr K. Smith for his considerable photographic work; Mr N. Mudford for his assistance with the shock tube experiments and many constructive discussions; Mr K. Crane for providing the results of his work; Messrs J. Baird, M. Daffey, N. Ebrahim who readily gave me assistance when it was necessary; the staff at the ANU Computer Centre and my mother for her excellent typing of this thesis.

I wish to express my appreciation to the Australian National University for awarding me an ANU Ph.D. scholarship to undertake this study.

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 H_2 dissociation 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 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 H_2 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-exciting 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.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

ABSTRACT

CHAPTER 1. INTRODUCTION

1.1	Aim	1
1.2	Historical Review	2
1.2.1	Vibrational Relaxation	2
1.2.2	Chemical Relaxation	8
1.3	Planned Research	13
1.3.1	Vibrational Relaxation	14
1.3.2	Chemical Relaxation	15
1.4	Outline of Thesis	16

CHAPTER 2. THEORY

2.1	Introduction	18
2.2	Diatomic Relaxation Model	18
2.2.1	The Vibrational Master Equation	20
2.2.2	Transition Probabilities	22
2.3	First Moment Solution	25
2.3.1	Method	25
2.3.2	Comparison with Experiment	28
2.4	Full Solution	29
2.4.1	Heat Bath	31
2.4.2	Normal Shock	34
2.4.3	Nozzle Flow	37
2.5	Summary of Theoretical Results	39
2.6	Conventional Methods of Solving Relaxation Rate Problems	40
2.6.1	Thermodynamic Model	40
2.6.2	Normal Shock	43
2.6.3	Nozzle Flow	46
2.6.4	Wedge Flow	48
2.6.4.1	Shock Curvature	49
2.7	Summary	51

CHAPTER 3. EXPERIMENT

3.1	Introduction	52
3.2	DDT Shock Tube Experiments	52
3.2.1	Relaxation Rate Model and Numerical Calculations	54
3.2.2	Experiment	57
3.2.3	Results	58
3.2.4	Summary	62

3.3	T2	Shock Tunnel Experiments	63
	3.3.1	Relaxation Rate Model and Numerical Calculations	65
	3.3.2	Experiment	67
	3.3.3	Results	71
		3.3.3.1 Shock Angle Measurements	71
		3.3.3.2 Shock Curvature Measurements	74
	3.3.4	Summary	76
3.4	T3	Shock Tunnel Experiments	77
	3.4.1	Relaxation Rate Model and Numerical Calculations	80
	3.4.2	Experiment	82
	3.4.3	Results	83
		3.4.3.1 Analysis of Mass-Spectrometer Results obtained by Crane (1975)	83
		3.4.3.2 Results with 35 degree Wedges	85
		3.4.3.3 Initial Shock Curvature	88
		3.4.3.4 Calculation of the Flow Field	92
	3.4.4	Summary	94
3.5		Summary of Experimental Results	94
CHAPTER 4. CONCLUSIONS			
4.1		Thesis Results	96
4.2		Suggestions for Further Related Research	98
REFERENCES			101
LIST OF SYMBOLS			109
FIGURES Part1 , Part2			