

CONTENTS

Chapter	Page
PREFACE	ix
1. QUANTUM THEORY	1
1.1 The real gas	1
1.2 The regime of the real gas	2
1.3 The quantum concept and its experimental verification	3
1.4 Bohr's theory of the atom and molecule	6
1.5 Matrix mechanics	9
1.6 Wave mechanics and wave packets	9
1.7 Wave mechanics of atoms and molecules	12
1.8 The meaning of ψ and the Heisenberg uncertainty principle	15
1.9 Operators in wave mechanics	18
1.10 Angular momentum	20
1.11 Wave mechanics of complex atoms and molecules	21
1.12 The Born–Oppenheimer approximation in molecules	23
1.13 Electronic states of an atom	24
1.14 Homopolar valence bonding	29
1.15 Quantum numbers of a molecule	31
1.16 The Wigner–Witmer rules	34
2. THERMODYNAMICS	37
2.1 Thermal equation of state	37
2.2 Mixtures of thermally perfect gases	38
2.3 The laws of thermodynamics. Some necessary definitions	40
2.4 The first law of thermodynamics	41
2.5 Reversible and irreversible processes	42
2.6 The second law of thermodynamics and entropy	43
2.7 Work	44
2.8 The thermodynamic equation	45
2.9 Other forms of the thermodynamic equation	46
2.10 Mixtures of thermally perfect gases	48
2.11 Chemical reactions and equilibria	51
3. STATISTICAL MECHANICS	57
3.1 Entropy and probability	58
3.2 Quantum statistical mechanics	59
3.3 A simple thermodynamic system	60
3.4 The most probable state	62
3.5 Entropy of the system	63
3.6 Gaseous systems	64
3.7 Partition functions	66
3.8 Factorization property of partition functions	68
3.9 Translational motion	70
3.10 Rotational motion. Diatomic molecules	74

CONTENTS

Chapter		Page
3.11	Vibrational energy and dissociation	76
3.12	Electronic and nuclear energy	81
3.13	Caloric equations of state and specific heats of pure gases	82
3.14	Mixed gases and chemical equilibrium	86
3.15	The dissociating homonuclear diatomic gas	91
3.16	The ideal dissociating gas	93
3.17	Molecular velocities. The Maxwellian distribution	96
4.	CHEMICAL REACTION RATES	100
4.1	Reaction rates and chemical times	100
4.2	The symmetrical diatomic gas	103
4.3	The reaction rate constant	104
4.4	The absolute theory of reaction rates	109
4.5	The steric factor	115
4.6	Relaxation of a two quantum level molecular gas	116
5.	NON-EQUILIBRIUM THEORY	119
5.1	The Boltzmann equation	120
5.2	Molecular velocities and fluxes	122
5.3	The equations of change	128
5.4	Molecular collisions	134
5.5	Molecular collisions (continued)	138
5.6	Equilibrium solutions	140
5.7	Series solution of the Boltzmann equation	142
5.8	Some special cases	152
5.9	The Eucken-corrected thermal conductivity	155
5.10.	Elementary kinetic theory	157
6.	THEORETICAL GAS DYNAMICS	165
6.1	A general thermodynamic equation	165
6.2	The entropy equation	170
6.3	Mass conservation equation	175
6.4	Entropy rise due to chemical reactions	179
6.5	Sound propagation in an ideal dissociating gas	182
6.6	Acoustic approximations	191
6.7	Stagnation enthalpy and vorticity	201
6.8	Characteristics	203
6.9	Shock waves (introduction)	210
6.10	The fully dispersed shock wave	216
6.11	Bulk viscosity and relaxation times	223
6.12	Partly dispersed wave. Relaxation zones	225
6.13	Equations of change in a one-dimensional steady flow	227
6.14	Relaxation zone in a dissociating diatomic gas	229
6.15	Equilibrium conditions behind a shock wave	235
6.16	Nozzle flows	240
6.17	Energy transfer. Accommodation effects	244
6.18	Energy flux through a pure polyatomic gas	249
6.19	Heat transfer through a reacting mixture	259

CONTENTS

Chapter	Page
7. THE PHYSICS OF GAS DYNAMICS	275
7.1 Collisions in hot gases	275
7.2 Types of inelastic collisions	276
7.3 The wave mechanical calculation of the differential scattering cross section	277
7.4 The incident partial waves	278
7.5 Angular momentum in atomic collisions	279
7.6 The scattered wave	281
7.7 The significance of the phase shifts	282
7.8 Quantum and classical elastic scattering cross sections	283
7.9 The inelastic scattering problem	284
7.10 The Born approximation	285
7.11 Other approximate solutions to the inelastic collision problem	286
7.12 The method of distorted waves	289
7.13 The method of perturbed stationary states	289
7.14 Ehrenfest's adiabatic principle applied to inelastic collisions	290
7.15 The shock tube	292
7.16 The importance of vibrational relaxation	296
7.17 Derivation of the multi-quantum level population equation	296
7.18 The relaxation equation for a system of simple harmonic oscillators	298
7.19 Relationships between the relaxation time and the parameters of kinetic theory and quantum theory	300
7.20 The Landau-Teller theory using the older quantum mechanics	300
7.21 The role of the intermolecular potential in the energy transfer process	302
7.22 Wave mechanical calculations of collisional transition probability	303
7.23 Adiabatic perturbation treatment of the intermolecular potential	304
7.24 The wave mechanical calculations of Mott and Jackson	306
7.25 The wave mechanical calculations of Herzfeld and co-workers	307
7.26 Improvements in the analysis	308
7.27 The complete classical theory for the transition probability	309
7.28 The wave mechanical calculations of Bauer and Salkoff	310
7.29 Wave mechanical calculations of Widom	312
7.30 Vibrational relaxation in a pure diatomic gas	313
7.31 The Landau-Teller graphical plot of relaxation time	314
7.32 Experimental studies of vibrational relaxation	316
7.33 Objections to macroscopic determination of vibrational relaxation times	317
7.34 Vibrational relaxation studies using emission and absorption techniques	319
7.35 The theoretical relaxation studies of Shuler and his collaborators	322
7.36 Solution of the vibrational relaxation Master Equation	326
7.37 Rotational and vibrational relaxation studies of Shuler <i>et al.</i>	329
7.38 Rotational relaxation transition probabilities	331
7.39 Experimental studies of rotational relaxation	332
7.40 Vibrational relaxation in a thermally isolated system	333
7.41 Further comments on experimental studies of vibrational relaxation	335

CONTENTS

Chapter	Page
7.42 Further comments on relaxation within an internal energy mode	338
7.43 Available energy theory of dissociation	339
7.44 Improvements in the available energy theory	340
7.45 Kinetics of dissociation	342
7.46 The 'climbing the ladder' theory of dissociation	343
7.47 The multi-level quantum jump theory of dissociation	348
7.48 The recombination process	349
7.49 The Rabinowitch collision theory of recombination	352
7.50 The recombination collision theory of Marshall and Davidson	354
7.51 Keck's statistical theory of recombination	356
7.52 Bunker's analysis of the recombination Mechanism 1	358
7.53 Absolute reaction rate theory of dissociation	360
7.54 Wigner's theory of recombination	361
7.55 Keck's variational theory of recombination	362
7.56 Dissociation and recombination in a vibrationally relaxing gas	365
7.57 Experimental studies of dissociation and recombination in diluted gases	368
7.58 Experimental studies of dissociation and recombination in pure gases	372
7.59 Collisions involving electronically excited molecules	374
7.60 Quantum theory of chemical reactions	377
7.61 Non-equilibrium chemical reactions	379
7.62 Dissociation as a non-equilibrium chemical reaction	383
7.63 Imperfect gases and the intermolecular potential	386
7.64 Radiation from atoms	390
7.65 Radiation from molecules	392
7.66 Radiative transition probabilities	393
7.67 Selection rules	402
7.68 Molecular spectra (continued)	403
7.69 Molecular transition probabilities	404
7.70 Radiation from hot air	406
7.71 Non-equilibrium radiation	409
INDEX	415