

# MOLECULAR THEORY

*of*

# GASES *and* LIQUIDS

**Joseph O. Hirschfelder**

DEPARTMENT OF CHEMISTRY AND  
THEORETICAL CHEMISTRY INSTITUTE  
UNIVERSITY OF WISCONSIN

**Charles F. Curtiss**

DEPARTMENT OF CHEMISTRY AND  
THEORETICAL CHEMISTRY INSTITUTE  
UNIVERSITY OF WISCONSIN

**R. Byron Bird**

DEPARTMENT OF CHEMICAL ENGINEERING  
UNIVERSITY OF WISCONSIN

PHYSIKALISCHE BIBLIOTHEK  
FACHBEREICH 5  
TECHNISCHE HOCHSCHULE  
DARMSTADT

Corrected Printing with Notes Added

With the assistance of the staff of the former  
University of Wisconsin Naval Research Laboratory

**JOHN WILEY & SONS, INC.**  
NEW YORK • LONDON • SYDNEY

# CONTENTS

NOTE ON NOTATION	xxi
VECTOR AND TENSOR NOTATION	xxiii
CHAPTER 1. INTRODUCTION AND BACKGROUND INFORMATION	1
1. The Equation of State—The Virial Coefficients	1
a. An ultra-simplified theory of the equation of state of dilute gases	2
b. An ultra-simplified theory of the equation of state of dense gases and liquids	4
c. Introduction to the statistical mechanical theory of the equation of state	6
2. The Kinetic Theory of Gases—The Transport Coefficients	8
a. An ultra-simplified kinetic theory of dilute gases	9
b. Introduction to the rigorous kinetic theory of gases	17
c. The equations of change and their applications	21
3. Intermolecular Forces—Intermolecular Potential Energy Functions	22
a. Sources of information about intermolecular forces	23
b. Contributions to the intermolecular forces	25
c. Empirical intermolecular potential functions	31
4. Classical Mechanics	35
a. Equations of motion in classical mechanics	36
b. The Liouville equation	40
c. The virial theorem	41
5. Molecular Collisions in Classical Mechanics	43
a. Summational invariants of an encounter	43
b. The trajectories of the individual particles during a collision	45
c. The angle of deflection in a collision	50
6. Quantum Mechanics	52
a. Experimental manifestations of non-classical behavior	52
b. Wave-mechanical description of systems	53
c. Operators in wave mechanics	56
d. Indistinguishability of identical particles	59
e. Approximation methods for solving the Schrödinger equation	61
f. The quantum mechanical virial theorem	68
7. Molecular Collisions in Quantum Mechanics	69
a. Interaction of two-particles: the phase shifts	69
b. Probability of an angle of deflection	72
PART I. EQUILIBRIUM PROPERTIES	
CHAPTER 2. STATISTICAL MECHANICS	79
1. Description of Statistical Ensembles in Classical Mechanics	79
a. Configuration, momentum, and phase spaces	80
b. Ensembles and distribution functions	82

c. The change with time of the probability density	84
d. Ensembles which represent closed systems in equilibrium	85
e. Ensembles which represent open systems in equilibrium	87
2. Description of Statistical Ensembles in Quantum Mechanics *	88
a. Quantum mechanical treatment of single systems	88
b. Definition of the probability density matrix	89
c. The physical significance of the density matrix	91
d. Other probability densities	92
e. Time-dependence of density matrix; equilibrium ensembles for closed systems	93
f. Equilibrium ensembles for open systems	94
3. The Basis of Statistical Mechanics	94
a. Justification of the microcanonical ensemble	95
b. The distribution of energy among macroscopic subsystems	95
c. Ensemble averages and fluctuations	98
d. The distribution of energy among molecules in a gas	100
e. Justification for the use of the canonical ensemble	101
f. Calculation of ensemble averages	103
4. The Fundamentals of Statistical Thermodynamics	105
a. The partition function	105
b. The internal energy and the first law of thermodynamics	106
c. Temperature and entropy and the second law of thermodynamics	107
d. Entropy at absolute zero and the third law of thermodynamics	109
e. The thermodynamic properties in terms of the partition function	110
5. The Evaluation of the Thermodynamic Properties of Ideal Gases	111
a. The partition function for the ideal gas	111
b. Distribution of energy among the molecules of an ideal gas	112
c. Contributions to the thermodynamic properties	114
d. Ideal gas mixtures	120
6. The Theory of Fluctuations	121
a. Fluctuations in the density in terms of the thermodynamic properties	122
b. Fluctuations in the density in terms of the radial distribution function	127
CHAPTER 3. THE EQUATION OF STATE OF GASES AT LOW AND MODERATE DENSITIES	131
<i>(In collaboration with Dr. Ellen L. Spatz, University of Wisconsin)</i>	
1. Development of the Equation of State from Statistical Mechanics	132
a. The method of the partition function	133
b. The method based on the virial theorem of mechanics	134
c. Equivalence of the partition function and the virial theorem methods	136
2. The Virial Equation of State from the Partition Function	137
a. The " <i>U</i> -functions"	137
b. The cluster integrals, $b_l$	139
c. Evaluation of the partition function	141
d. The equation of state in the virial form	144
3. The Virial Equation of State from the Virial Theorem	145
a. The "modified <i>U</i> -functions"	145
b. The "modified cluster integrals"	146
c. The pair distribution function in terms of the density	146
d. The equation of state in the virial form	147

\* This section was written with the assistance of Professor J. de Boer, University of Amsterdam, The Netherlands.

4. The Virial Coefficients	148
a. The assumption of additivity	148
b. The virial coefficients for angle-independent potentials	150
c. The virial coefficients for angle-dependent potentials	151
d. The virial coefficients for mixtures	153
e. The determination of virial coefficients from equation of state data	154
5. Virial Coefficients for Simple Angle-Independent Potentials	156
a. Rigid spheres	156
b. Point centers of repulsion	157
c. The Sutherland model	158
d. The square-well potential	158
6. The Virial Coefficients for the Lennard-Jones (6-12) Potential	162
a. Calculation of the second virial coefficient	162
b. Determination of intermolecular forces from second virial coefficients	166
c. Evaluation of the third virial coefficient	170
d. The Joule-Thomson coefficient	173
7. The Second Virial Coefficient for More Elaborate Potentials	178
a. The Buckingham-Corner potential	178
b. The modified Buckingham (6-exp) potential	180
8. The Second Virial Coefficient for Non-spherical Molecules	183
a. Isihara's treatment of rigid convex molecules	183
b. Kihara's generalized sphero-cylindrical molecules	187
c. Kihara's generalized ellipsoidal molecules	190
d. Corner's four-center model for long molecules	193
9. Discussion of the Results for Several Non-polar Potential Functions	196
a. Spherical molecules	196
b. Non-spherical molecules	205
c. Comparison of different types of potential energy functions	206
10. The Virial Coefficients for Polar Gases *	209
a. Rigid spheres with imbedded point-dipoles	210
b. The second virial coefficient for the Stockmayer potential	211
c. Determination of the parameters in the Stockmayer potential	215
d. Joule-Thomson coefficients for the Stockmayer potential	217
e. The third virial coefficient for the Stockmayer potential	220
f. Calculations for mixtures	222
g. Dipole-quadrupole interactions in complex molecules	225
Appendix A. Kihara's Evaluation of the Third Virial Coefficient	228
Appendix B. Thermodynamic Properties in Terms of Virial Coefficients	230
CHAPTER 4. THE EQUATION OF STATE OF DENSE GASES AND LIQUIDS	234
1. The Principle of Corresponding States	235
a. The empirical principle of corresponding states	235
b. The Hougen and Watson generalized charts	239
c. The principle of corresponding states for spherical non-polar gases	244
d. The principle of corresponding states for polyatomic molecules	247
e. The principle of corresponding states for polar molecules	248
2. Empirical Equations of State	250
a. Two-constant equations of state	250
b. The Beattie-Bridgeman equation of state	253

\* This section was prepared with the assistance of Professor J. S. Rowlinson, Dept. of Chemical Eng., Imperial College, University of London.

c. The Benedict-Webb-Rubin equation of state	258
d. Empirical relations for liquids	261
3. Gases at Very High Pressures	262
a. An equation of state for powder gases	262
b. Equation of state behavior in detonations	263
c. Use of the virial theorem to study distortion of molecules	264
d. Quantum mechanical treatment of the distortion of molecules	268
e. Optical and electrical methods for studying the distortion of molecules	271
4. Some General Considerations about the Cell Methods	271
a. Crystal structure as the basis for cell methods	272
b. The concept of communal entropy	273
c. The concept of free volume	276
5. A Simple Cell Model for Liquids and Dense Gases	279
a. Approximate expressions for the free volume and the lattice energy	279
b. The Eyring equation of state	281
c. The vapor pressure: Hildebrand's rule and Trouton's rule	283
d. Heat capacities	284
e. The entropy change on melting	285
6. The Equation of State for Rigid Non-attracting Spheres	286
a. The exact and "smeared" free volume	286
b. The equation of state at low density: hard and soft center free volumes	290
7. The Equation of State of Lennard-Jones and Devonshire	293
a. Development of the equation of state	294
b. The three-shell modification	296
c. Comparison with experimental results	303
d. The double-occupancy modification	305
8. Hole Theories of Liquids and Dense Gases	311
a. General theory of holes in liquids	311
b. The linear approximation for the logarithm of the free volume	313
c. Comparison of hole theory calculations with experiment	316
9. The Equation of State in Terms of the Pair Distribution Function	320
a. Behavior of the pair distribution function	321
b. The "potential of the average force"	324
c. Derivation of integral equations for the pair distribution function	325
d. Solution of the integral equation: the superposition approximation	328
CHAPTER 5. VAPOR-LIQUID EQUILIBRIA AND CRITICAL PHENOMENA *	336
1. The Interfacial Region between a Liquid and a Vapor	337
a. Definition of surface tension	337
b. Surface tension from free-volume methods	342
c. Surface tension from the radial distribution function	347
d. Effect of radius of curvature on surface tension	348
e. First-order calculations of surface tension	352
f. Macleod's equation and the parachor	354
2. Phase Behavior of One-Component Systems	357
a. Methods of determining the critical point	357
b. Stable and metastable states	363

\* This chapter was prepared with the assistance of Dr. C. A. Boyd, Aero Projects, Inc., West Chester, Pa.

## CONTENTS

xiii

c. Thermodynamic properties in the critical region	367
d. Behavior of substances in the critical region *	372
e. Statistical mechanical theory of condensation	376
3. Phase Behavior of Two-Component Systems	380
a. The critical point and retrograde behavior	381
b. Thermodynamic considerations	388
Appendix. A. The Chemical Potential of a van der Waals Mixture	391
CHAPTER 6. QUANTUM THEORY AND THE EQUATION OF STATE	392
<i>(By J. de Boer and R. Byron Bird)</i>	
1. Statistical Mechanical Preliminaries	393
a. The probability density matrix for the canonical ensemble	393
b. The probability density matrix in the classical limit	395
2. Development of the Equation of State from Statistical Mechanics	398
a. The method of the partition function	398
b. The method based on the virial theorem of quantum mechanics	399
c. Equivalence of the partition function and the virial theorem methods	400
d. Final expressions for the quantum mechanical equation of state	400
3. The Properties of a Perfect Gas	401
a. The Slater sum for a perfect gas composed of molecules with zero spin	401
b. The Slater sum for a perfect gas composed of molecules with non-zero spin	403
c. The equation of state for a perfect gas	404
d. Bose-Einstein condensation	405
4. The Second Virial Coefficient at Very Low Temperatures	407
a. The second virial coefficient in terms of phase shifts	407
b. Phase shifts for simple potentials	410
c. Calculations for the Lennard-Jones potential	413
5. The Second Virial Coefficient at "Intermediate" Temperatures	419
a. Expressions for the quantum deviations of the second virial coefficient	419
b. Series expressions for the quantum deviations of $B(T)$	420
c. Calculations for the Lennard-Jones potential	422
d. Calculations for the Buckingham-Corner potential	424
6. The Principle of Corresponding States in Quantum Mechanics	424
a. Statement of the principle of corresponding states in quantum mechanics	424
b. Quantum effects in the liquid phase	426
c. The properties of the isotopes of helium and hydrogen	431
7. Quantum Effects in Diatomic Gases	434
a. Brief summary of the theoretical development	434
b. Comparison of theory and experiment for hydrogen	436

## PART II. NON-EQUILIBRIUM PROPERTIES

CHAPTER 7. THE KINETIC THEORY OF DILUTE GASES	441
1. The Kinetic Theory Distribution Functions	442
a. Physical description of non-equilibrium systems	442
b. Physical derivation of the Boltzmann equation	444

\* This discussion was prepared with the assistance of Professor H. B. Palmer, Dept. of Fuel Technology, Pennsylvania State University.

c. The Boltzmann equation from the Liouville theorem	449
d. The distribution in velocities	452
2. The Equations of Change	453
a. Molecular velocities and stream velocities	453
b. The flux vectors	455
c. The general equations of change	459
d. Vanishing of the collision integrals for the summational invariants	460
e. Explicit expressions for the equations of change	461
3. Enskog's Solution of the Boltzmann Equation	464
a. The $H$ -theorem (the equilibrium solution)	464
b. The Enskog series	466
c. The first-order perturbation solution	468
d. The integral equations	469
e. Several important integral theorems	472
f. Establishment of a variational principle	474
g. Application of the variational principle (the Sonine polynomial expansion)	475
4. The Formulation of the Transport Coefficients	478
a. Coefficients of diffusion and thermal diffusion	478
b. Coefficient of viscosity	480
c. Coefficient of thermal conductivity	481
d. The integrals $\Omega^{(l,s)}$	484
e. Explicit formulae for the transport coefficients in terms of the $\Omega^{(l,s)}$	485
5. Grad's Solution of the Boltzmann Equation	492
a. The moment equations	493
b. The "thirteen-moment" approximation	494
6. Effects of Chemical Reactions and Internal Degrees of Freedom	496
a. The equations of change for a reacting gas mixture	496
b. The effect of internal degrees of freedom (the Eucken correction)	498
c. The formal kinetic theory of polyatomic molecules	501
d. Several special models (rigid ovaloids, rough spheres, loaded spheres)	506
Appendix A. Bracket Expressions in Terms of the $\Omega^{(l,s)}$	511
CHAPTER 8. TRANSPORT PHENOMENA OF DILUTE GASES	514
(In collaboration with Dr. Ellen L. Spatz, University of Wisconsin)	
1. The Flux Vectors and the Transport Coefficients	515
a. Mass transfer and the diffusion coefficients	516
b. Momentum transfer and the viscosity coefficients	521
c. Energy transfer and the thermal conductivity coefficient	522
2. Summary of Kinetic Theory Formulae for Pure Gases and Mixtures	523
a. The quantities $\Omega^{(l,s)}$ *	523
b. The coefficient of viscosity	528
c. The coefficient of thermal conductivity	533
d. The coefficient of diffusion	538
e. The coefficient of thermal diffusion	541
3. Transport Coefficients for Simple Potentials	543
a. Rigid elastic spheres	544
b. Point centers of repulsion	546
c. The Sutherland model	549
d. The square-well potential	551

4. Transport Coefficients for the Lennard-Jones (6-12) Potential	552
a. The dynamics of a collision; calculation of cross-sections	553
b. The coefficient of viscosity of pure gases	560
c. The coefficient of viscosity of mixtures	566
d. The coefficient of thermal conductivity	573
e. The coefficient of diffusion	578
f. The thermal diffusion ratio	582
5. Comparison of Several Spherical Non-polar Potential Functions	589
6. Transport Coefficients for Polar Gases and Gas Mixtures	597
a. Viscosity of pure gases	597
b. Viscosity and diffusion for mixtures containing one polar component	600
Appendix A. Higher Approximations to the Transport Coefficients	604
CHAPTER 9. THE TRANSPORT PROPERTIES OF DENSE GASES AND LIQUIDS	611
1. The Principle of Corresponding States	613
a. Experimental observations of the transport properties at high densities	613
b. A principle of corresponding states for spherical non-polar molecules	617
c. Applications of the principle of corresponding states	619
d. The principle of corresponding states for polar molecules	622
2. The Eyring Theory of Transport Phenomena	624
a. The coefficient of viscosity	625
b. The coefficient of diffusion	631
c. The coefficient of thermal conductivity	633
3. The Enskog Theory of Transport Phenomena	634
a. The Boltzmann equation as modified for a dense gas	636
b. The flux vectors	638
c. The equations of change	640
d. The solution of the modified Boltzmann equation	642
e. The transport coefficients	643
f. Summary of results for rigid spheres	647
g. Application of results to real gases	649
4. The Transport Properties from Statistical Mechanics	652
a. The Liouville equation and the general equation of change	653
b. The macroscopic variables	654
c. The macroscopic variables in terms of lower-order distribution functions	655
d. The flux vectors and the equations of change	657
e. Calculation of the transport coefficients	659
Appendix A. The Eyring Theory of Reaction Rates	661
CHAPTER 10. QUANTUM THEORY AND TRANSPORT PHENOMENA	668
<i>(By J. de Boer and R. Byron Bird)</i>	
1. Non-equilibrium Quantum Statistical Mechanics	669
a. General statistical mechanical theory	669
b. The Boltzmann equation for dilute gas mixture	671
2. Transport Phenomena at Very Low Temperatures	674
a. The diffraction effects	675
b. The symmetry effects	677
c. Calculations at very low temperatures	680
3. Transport Phenomena at Intermediate Temperatures	684
a. The WKB development of the phase shifts	685

b. The cross-sections as power series in Planck's constant	687
c. Calculations for an inverse twelfth-power repulsive potential	690
4. The Principle of Corresponding States in Quantum Mechanics	692
CHAPTER 11. HYDRODYNAMIC APPLICATIONS OF THE EQUATIONS OF CHANGE	694
1. The Hydrodynamic Equations	695
a. Applicability of the equations of change	695
b. Summary of the equations of change	698
c. The equation of change of entropy	700
2. The Thermodynamics of Irreversible Processes	704
a. The Onsager reciprocal relations	705
b. Application to the transport phenomena	708
c. Application to momentum transport	710
d. Application to mass and energy transport	712
e. Summary of results	717
3. Energy Transfer by Radiation	720
a. Radiation flux for two special cases	723
b. Stationary radiation front	726
4. The Theory of Sound Propagation	728
a. Propagation without absorption	728
b. Propagation with absorption	730
5. The Propagation of Finite Waves in One Dimension	736
a. The Riemann method of characteristics	736
b. Application of the method of characteristics to a perfect gas	740
c. The formation of shock waves in a perfect gas	742
6. One-Dimensional Steady-State Equations of Change	746
a. The basic equations for a system under general conditions	747
b. The basic equations for a system near equilibrium	751
7. The Theory of Flame Propagation	756
a. Qualitative discussion of the Bunsen burner flame	757
b. The theory of steady-state one-dimensional flame propagation	761
c. Simple example of a flame (unimolecular reversible reaction)	766
d. Simple example of a flame: kinetic energy and diffusion neglected	770
e. Simple example of a flame: kinetic energy neglected but not diffusion	775
f. Simple example of a flame: diffusion neglected but not kinetic energy	780
8. The Theory of Shock Wave Propagation	783
a. The Hugoniot relations	785
b. Application of the Hugoniot relations to a perfect gas	786
c. The structure and thickness of a shock wave in a perfect gas	791
9. The Theory of Detonations	797
a. The Hugoniot relations and the Chapman-Jouguet condition	797
b. Applications of the theory of detonations to perfect gases	803
c. The structure of a detonation wave	807
10. The Flow of Propellant Gases in Rockets	814
a. The equations of change	815
b. Applications to a perfect gas	818
c. The thermochemistry of real gas mixtures	821
d. The flow of a real gas through a nozzle	825

## PART III. INTERMOLECULAR FORCES

CHAPTER 12. ELECTROMAGNETIC BASIS OF INTERMOLECULAR FORCES	835
1. Electrostatics	836
a. Coulombic interaction between charges and charge distribution	836
b. The electrostatic potential and the electric field intensity	838
c. Multipole moments	839
d. The "one-center" expansion	841
e. The "two-center" expansion	843
f. Behavior of electric dipoles	846
2. Polarization of Matter and the Electric Susceptibility	851
a. Polarizability and polarization	852
b. The $\mathcal{D}$ and $\mathcal{E}$ fields	853
c. The local field, $\mathcal{E}^{(loc)}$	855
d. Electric susceptibility in terms of the dielectric constant	857
e. The electric susceptibility in terms of the molecular properties	859
3. Maxwell's Equations of Electromagnetism	862
a. Maxwell's equations in a vacuum	863
b. The scalar and vector potentials; magnetic multipoles	865
c. The magnetization of matter	867
d. Maxwell's equations for a material medium	869
4. Magnetization of Matter and the Magnetic Susceptibility	871
a. The $\mathcal{H}$ and $\mathcal{B}$ fields	871
b. The local field $\mathcal{B}^{(loc)}$	874
c. The magnetic susceptibility in terms of the magnetic permeability	875
5. Classical Theory of Light Absorption and the Index of Refraction	877
a. The oscillating dipole (the Hertzian oscillator)	878
b. The equation of motion of charged particles	880
c. The index of refraction (Drude's theory)	881
6. Quantum Theory of Light Absorption and the Index of Refraction	883
a. Transition probabilities for a molecule in an electromagnetic field	883
b. Induced absorption and emission of light	885
c. The index of refraction	888
7. Scattering of Electromagnetic Waves	891
a. Scattering of visible light	894
b. Scattering of x-rays	898
Appendix A. The Two-Center Expansion Coefficients	900
Appendix B. The Representation Coefficients of the Three-Dimensional Rotation Group	905
Appendix C. Matrix Components of the Dipole Moment for Optical Transitions	912
CHAPTER 13. THE THEORY OF INTERMOLECULAR FORCES	916
1. Intermolecular Potential Energy Functions	919
a. The concept of an intermolecular potential energy function	919
b. Separation of electronic and nuclear motions (Born-Oppenheimer separation)	925
c. Information about intermolecular potentials from the virial theorem	930
d. Equivalence of classical and quantum mechanical intermolecular forces	932

e. Quantum mechanical calculation of the intermolecular potential energy	937
2. The Polarizability of Molecules	941
a. Variational method for the calculation of polarizabilities	942
b. The polarizability of molecular hydrogen	946
c. The additivity of bond polarizabilities	947
d. Polarizability and other properties of atoms from screening constants	951
3. The London Dispersion Forces between Symmetrical Molecules	955
a. A simplified theory of dispersion forces based upon the Drude model	956
b. Second-order perturbation treatment of dispersion forces	960
c. Higher terms in the expression for the dispersion energy	964
d. The influence of "retardation" on the dispersion forces at large distances	967
4. Dispersion Forces between Asymmetric Molecules	968
a. Dispersion forces between asymmetric molecules at large separations	969
b. Dispersion forces between asymmetric molecules at intermediate separations	970
c. Energy of dispersion between long conjugated double-bond molecules	974
5. Forces between Molecules Having Permanent Electric Moments	983
a. The energy of induction	984
b. The potential energy of interaction averaged over orientations	985
c. The relative magnitude of the contributions to the intermolecular potential	988
d. Hydrogen bonds as electrostatic forces	989
6. Quantum Treatment of Resonance and Electrostatic Forces	990
a. The nature of resonance forces	991
b. Quantum interaction of two ideal dipoles in linear molecules	997
c. Quantum interaction between two ideal dipoles in symmetrical tops	1004
d. Long-range interactions between a proton and a hydrogen or helium atom	1007
e. Quadrupole-quadrupole forces between atoms not in <i>S</i> -states	1013
7. Intermolecular Forces from Microwave Spectra	1020
a. The broadening of lines in microwave spectra	1021
b. Information about long-range forces from pressure broadening	1025
8. Determination of the Quadrupole Moment of the Water Molecule	1029
a. Theoretical determination	1030
b. Empirical determination	1033
9. Intermolecular Forces from Properties of Crystals	1035
a. The potential energy of the crystal lattice	1036
b. The zero-point energy of the crystal lattice	1041
c. Determination of the forces between noble gas atoms	1042
Appendix A. Complete Hamiltonian for a System in External Electric and Magnetic Fields	1044
Appendix B. The Ratio of Kinetic to Potential Energy of Electrons in a Molecular System	1046
<b>CHAPTER 14. QUANTUM MECHANICAL CALCULATIONS OF INTERMOLECULAR FORCES</b>	<b>1050</b>
1. The Interaction between Two Hydrogen Atoms	1054
a. The $^1\Sigma$ state corresponding to the normal $H_2$ molecule	1059
b. The $^3\Sigma$ state corresponding to repulsion of two <i>1s</i> hydrogen atoms	1062
2. The Energy of Interaction between Noble Gas Atoms	1064
a. Interaction of two helium atoms	1064

## CONTENTS

xix

b. Interaction of two neon atoms	1070
c. Interaction of two argon atoms	1073
3. Interaction of a Hydrogen Atom with a Hydrogen Molecule	1075
a. Eyring semi-empirical method	1076
b. Direct first-order perturbation and dispersion energy calculation	1080
4. Interaction between Two Hydrogen Molecules	1083
a. The chemical or valence energy	1083
b. The long-range energy of interaction	1086
c. The total interaction energy and comparison with experiment	1090
5. Interaction of H and H <sub>2</sub> with Various Hydrogen Ions	1092
a. The interaction H + H <sup>+</sup>	1092
b. The interaction H + H <sup>-</sup>	1094
c. The interactions H + H <sub>2</sub> <sup>+</sup> , H <sub>2</sub> + H <sup>+</sup> , and H <sub>2</sub> + H <sub>2</sub> <sup>+</sup>	1095
d. The interaction H <sub>2</sub> + H <sup>-</sup>	1096
e. Cluster of ions	1097
6. Interaction of He with an Excited He Atom or a Proton	1098
a. The interaction of a normal and a metastable helium atom	1098
b. The interaction of a normal helium atom with a proton	1102
Appendix A. Integrals Useful in the Calculation of Intermolecular Energies	1104
APPENDIX (TABLES)	1109
SYMBOLS AND NOTATION	1181
NOTES ADDED IN SECOND PRINTING (N)	1187
CHEMICAL INDEX	1217
AUTHOR INDEX	1219
SUBJECT INDEX	1229