

CONTENTS

Preface	xv
How to use the workbooks, exercises, and problems	xxi
Chapter 1 The fundamental equations of statistical mechanics	1
Introduction	1
<i>Why you need statistical mechanics</i>	1
<i>Why this theory is statistical: a discussion based on classical mechanics</i>	3
<i>Why we use statistical method: a quantum mechanical discussion</i>	5
The fundamental equations	6
<i>The fundamental equations are guesses</i>	6
<i>The fundamental equations: the probability that the system is in a specific state</i>	6
<i>The fundamental equations: connection to thermodynamics</i>	8
<i>Formulae for other thermodynamic quantities</i>	8
<i>Summary of the recipe for calculating thermodynamic functions</i>	11
<i>Classical statistical mechanics</i>	11

Chapter 2	The physical interpretation of the fundamental equations of statistical mechanics	13
	Introduction	13
	An operational definition of probability	14
	<i>We can use probabilities only to examine a large number of random events</i>	15
	<i>Fluctuations</i>	17
	The properties of P_α	19
	A few examples of populations and their use	22
	<i>A diatomic molecule embedded in a solid</i>	22
	<i>K₂ molecules inside a solid</i>	23
	<i>Application: emission spectroscopy</i>	24
	<i>Absorption spectroscopy</i>	27
	<i>Matrix isolation spectroscopy</i>	27
	<i>Night vision glasses</i>	28
Chapter 3	Interpretation of the thermodynamic quantities	31
	Energy	33
	Pressure	34
	<i>Dependence of E_α on N and V</i>	36
	Work and heat	38
	Entropy	40
	<i>A new equation for entropy</i>	40
	<i>What I mean by order</i>	41
	<i>The connection to statistical mechanics</i>	43
	<i>The dependence of entropy on temperature</i>	43
	The Third Law of Thermodynamics	46
Chapter 4	The partition function of a system of independent particles	49
	<i>If the total energy is a sum, the partition function is a product</i>	52
	<i>A correction for identical particles</i>	52

	<i>Stirling's approximation</i>	53
	<i>Is the free energy of a system of N noninteracting molecules equal to N times the free energy of one molecule?</i>	54
Chapter 5	The partition function of an ideal gas of atoms	57
	The translational partition function	59
	<i>Very small boxes</i>	66
	<i>About sums and integrals</i>	67
	The nuclear partition function q_n	67
	The electronic partition function q_e	68
	The choice of zero energy	70
Chapter 6	The thermodynamic functions of an ideal gas of atoms	73
	Introduction	73
	Helmholtz free energy	74
	<i>By dividing Q by $N!$, A has the correct dependence on V and N</i>	74
	<i>The free energy is a sum of a collective, a translational, an electronic, and a nuclear contribution</i>	75
	The energy U	76
	<i>The translational contribution U_t to energy</i>	77
	<i>The mean velocity</i>	78
	<i>Joule's experiments</i>	78
	<i>The electronic contribution U_e</i>	79
	<i>The total energy</i>	80
	Pressure	80
	Entropy	81
	<i>Nuclear contribution to entropy</i>	81
	<i>Translational contribution to entropy</i>	82
	<i>Electronic contribution to entropy</i>	83
	<i>Collective contribution to entropy</i>	84
	<i>The total entropy</i>	84

	The heat capacities C_v and C_p	85
	<i>The translational contribution</i>	86
	<i>The electronic contribution to C_v</i>	86
	The chemical potential	87
	<i>The translational contribution to μ</i>	88
	<i>The nuclear contribution to μ</i>	88
	<i>The electronic contribution to μ</i>	88
	<i>The collective contribution to μ_c</i>	89
	<i>The total chemical potential</i>	89
	<i>Chemical potential as a function of pressure</i>	90
	Summary	91
Chapter 7	The thermodynamics properties of an ideal gas for which electronic and nuclear contributions are negligible	93
	<i>Qualitative observations</i>	94
	<i>Quantitative tests: entropy</i>	95
	<i>The change in enthalpy</i>	96
	<i>Chemical potential</i>	98
Chapter 8	A test of the theory for a gas for which electronic and nuclear degrees of freedom matter	103
	Introduction	103
	Comparison with experiment: the method of computation and the results	106
	<i>Implementation</i>	107
	<i>The entropy of a gas of oxygen atoms: comparison to experiment</i>	108
	<i>The heat capacity</i>	108
	<i>The chemical potential: comparison to experiment</i>	110
	Supplement 8.1 A recipe for calculating the thermodynamic functions when the electronic and nuclear degrees are included	111
	<i>The heat capacity</i>	111

<i>The entropy</i>	112
<i>The chemical potential</i>	112
Chapter 9 The statistical mechanics of a gas of diatomic molecules	113
Introductory remarks and general preparation	113
<i>The partition function</i>	115
<i>The role of electronic excitations</i>	117
<i>The effect of nuclear degrees of freedom</i>	117
<i>The thermodynamic functions are sums of vibrational, rotational, and translational contributions</i>	118
Translational contributions to thermodynamic quantities	119
<i>The translational partition function q_t</i>	119
The vibrational contribution to thermodynamic quantities and the population of the vibrational states	121
<i>No measurable quantity changes if a constant to all energies</i>	121
<i>The choice of the vibrational energy</i>	122
<i>The vibrational partition function</i>	124
<i>A summary of the approximations made in calculating q_v</i>	126
<i>The vibrational temperature</i>	127
<i>Vibrational contribution to the thermodynamic functions</i>	128
<i>The probability of being in state v</i>	130
The rotational contribution to thermodynamic functions	131
<i>The rotational energy</i>	131
<i>The rotational partition function</i>	132
<i>The rotational partition function for homonuclear diatomics</i>	134
<i>Rotational contributions to thermodynamic quantities</i>	137
<i>The probability that a molecule is rotationally excited</i>	138
<i>Hot bands in spectroscopy</i>	139
<i>The contribution of the nuclear degrees of freedom</i>	140

Supplement 9.1 The rotational partition function for homonuclear diatomic molecules	143
Supplement 9.2 Symmetry requirements	144
<i>The total wave function must be symmetric or antisymmetric</i>	144
<i>The symmetry of the total wave function of a homonuclear diatomic molecule</i>	145
<i>The role of nuclear spin</i>	146
<i>Spin one-half</i>	147
<i>Fermions with arbitrary spin</i>	148
Supplement 9.3 The nuclear-rotational partition function of a homonuclear diatomic whose nuclei are fermions	149
<i>Symmetric nuclear-spin states</i>	149
<i>Antisymmetric nuclear-spin states</i>	149
<i>The total nuclear-rotational partition function of a homonuclear diatomic whose nuclei are fermions</i>	150
<i>High temperature limit</i>	151
<i>The temperature dependence of C_v for H_2</i>	153
<i>Taking symmetry into account for difference in the heat capacity</i>	154
<i>Orthohydrogen and parahydrogen</i>	155
Supplement 9.4 The nuclear-rotational partition function of a homonuclear diatomic whose nuclei are bosons	158
<i>Symmetry requirements for bosons</i>	158
Chapter 10 A gas of diatomic molecules: comparison with experiment	161
Introduction	161
A calculation of C_p and comparison to experiment	162
<i>A review of the equations for C_p</i>	162
<i>Qualitative features of the magnitude of C_p</i>	163
<i>The largest and smallest values of C_p</i>	165
<i>Comparison of the C_p of N_2 and K_2 to experiment</i>	167
<i>Results for K_2</i>	169
<i>The magnitude of C_p: Summary</i>	169

A comparison of the calculated entropy of O ₂ to experiment	172
Problems	176
Chapter 11 Chemical equilibrium	179
Introduction	179
A crude model of chemical equilibrium	180
<i>A simplified model</i>	180
<i>The equilibrium constant</i>	181
A statistical mechanical theory	185
<i>A review of thermodynamics</i>	186
<i>A statistical mechanical theory</i>	187
<i>The chemical potential of the gas of atoms</i>	187
<i>The chemical potential of the diatomic</i>	188
<i>Calculation of the equilibrium constant</i>	189
<i>The contributions from rotation, vibration, and translation</i>	190
How various quantities contribute to the equilibrium constant	191
<i>The translational contribution</i>	191
<i>Calculation of K_t</i>	192
<i>Vibrational contribution</i>	193
<i>Numerical results for the vibrational contribution</i>	194
<i>The role of rotational motion</i>	194
<i>The total equilibrium constants</i>	195
Chapter 12 Transition state theory: fundamental concepts	197
Introduction	197
<i>A review of chemical kinetics</i>	197
<i>The reaction requires energy and takes it from the environment</i>	199
The potential energy surface	200
<i>A chemical compound is a minimum on the potential energy surface</i>	200

<i>Most of the time a molecule's configuration is close to C_{mp}</i>	203
<i>Atoms having high kinetic energy tend to lose it</i>	204
<i>The potential energy surface of a molecule with two isomers</i>	205
<i>Between two minima there must be a ridge</i>	206
<i>What this has to do with chemical kinetics</i>	207
The dynamics of a chemical reaction	211
<i>To react, the molecule must cross an energy ridge</i>	211
<i>The energy causing a reaction comes from the medium</i>	212
<i>To cause a reaction, the energy must go into the right kind of motion: the reaction coordinate</i>	212
Chapter 13 Transition state theory: the motion of a chemisorbed atom along the surface	215
A description of a chemical reaction	215
<i>The structure of the system</i>	216
<i>The dynamics of the adsorbed atom</i>	217
<i>"Fast" for an adsorbed atom</i>	217
The potential energy surface of this system	219
<i>The energy reaction between two atoms</i>	219
<i>The potential energy surface</i>	220
<i>The energy of interaction of the adsorbed atom with the solid</i>	223
<i>The structure of the solid</i>	223
<i>The potential energy $V(\mathbf{r})$</i>	223
<i>The shape of $V(\mathbf{r})$</i>	225
<i>The symmetry of the surface and the position of the chemisorbed atom</i>	226
<i>The topology of the surface around the binding site</i>	227
<i>Adsorption and desorption</i>	228
<i>The shape of the potential energy surface around the fourfold binding site</i>	230

<i>Finding the coordinates of the transition state</i>	232
<i>The shape of the potential energy surface around the transition state</i>	234
Chapter 14 Transition state theory: the rate constant	237
Introduction	237
<i>Site-to-site hopping as a problem in kinetics</i>	238
<i>The rate equation</i>	239
The derivation of the rate equation and of a formula for the rate constant	240
<i>The dividing surface</i>	240
<i>The activated complex</i>	241
<i>The number of atoms forming an activated complex</i>	241
<i>The expression for the rate</i>	243
<i>The rate to escape from A</i>	244
<i>The rate constant</i>	247
<i>Calculating $k_{A \rightarrow B}$</i>	248
The rate constant $k_{B \rightarrow A}$; the detailed balance	249
Assumptions made by transition state theory	250
<i>Using equilibrium statistical mechanics to calculate N^*</i>	251
<i>Each atom is in an equilibrium state at all times</i>	252
<i>Why we have a reaction if everything is in equilibrium</i>	252
<i>Density fluctuations</i>	253
<i>Energy fluctuations and chemical reactions</i>	254
<i>Recrossing</i>	255
<i>Why the no-recrossing approximation works</i>	257
Supplement 14.1 The dividing surface in general	258
Chapter 15 Transition state theory: calculating the rate constant	261
Introduction	261
<i>A survey of the procedure for calculating $k_{A \rightarrow B}$</i>	261
The partition function q_A	262
<i>The harmonic approximation</i>	262

<i>The physical meaning of the terms in the harmonic expansion</i>	263
<i>The vibrational frequencies</i>	265
<i>The partition function q_A</i>	266
The partition function q^*	267
<i>The motion of the atom in the region A^*</i>	267
<i>The vibrational frequencies in the transition state</i>	268
<i>The partition function q^*</i>	269
The equation for the rate constant	269
<i>A review of the equation for $k_{A \rightarrow B}$</i>	270
<i>The temperature dependence of $k_{A \rightarrow B}$</i>	271
A numerical study of $k_{A \rightarrow B}$	271
<i>The temperature dependence of $k_{A \rightarrow B}$ is consistent with the Arrhenius formula</i>	271
<i>The isotope effect</i>	274
Summary	276
Appendices	279
A1. Values of some physical constants	279
A2. Energy conversion factors	280
Further Reading	281
Index	283