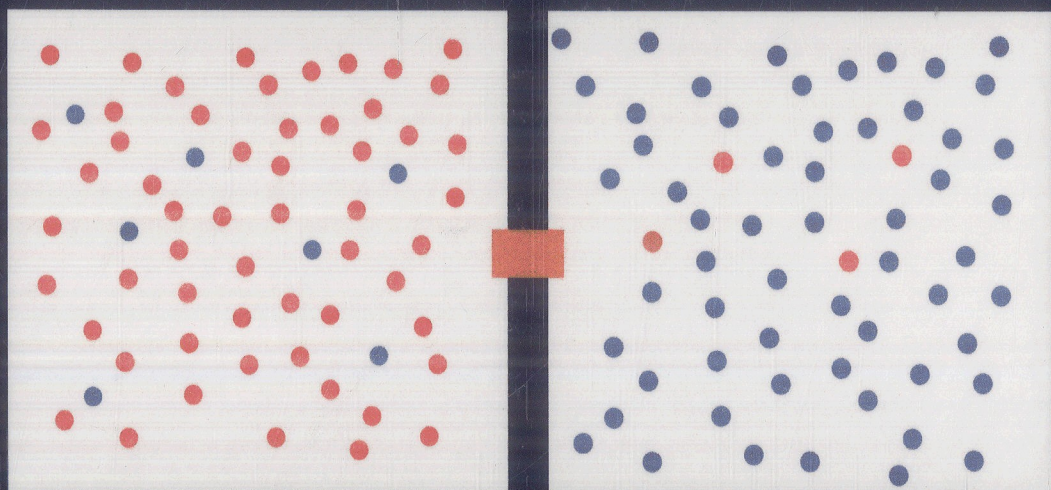


Michael E. Starzak

Energy and Entropy

Equilibrium to Stationary States



Springer

Contents

1	The First Law of Thermodynamics	1
1.1	The Conservation of Energy	1
1.2	Molar Heat Capacities	3
1.3	State Variables and Equations of State	5
1.4	Non-Ideal Gases	7
1.5	Work	9
1.6	Reversible Work	11
1.7	Work Cycles	14
1.8	Other Types of Work	15
1.9	Enthalpy	16
1.10	Heat Capacities as Partial Derivatives	18
	Problems	20
2	First Law Formalism	23
2.1	The Special Character of State Variables	23
2.2	Energy and Enthalpy for Chemical Reactions	24
2.3	Hess's Law and Reaction Cycles	26
2.4	Standard States	29
2.5	More Partial Derivatives	30
2.6	Generalized Thermodynamic Equations	32
2.7	Calculating Internal Energy	33
	Problems	35
3	First Law of Thermodynamics: Applications	37
3.1	General Equation for the First Law	37
3.2	The Joule Experiment	38
3.3	The Joule–Thomson Experiment	39
3.4	The Joule–Thomson Coefficient	40
3.5	The Reversible Isothermal Expansion	41
3.6	Irreversible Isothermal Expansion of an Ideal Gas	42
3.7	Isothermal Expansion of Non-ideal Gases	43
3.8	Adiabatic Reversible Expansions	45
3.9	Irreversible Adiabatic Expansion	47
	Problems	47

4	Entropy and the Second Law:	
	Thermodynamics Viewpoint	51
4.1	Temperature Gradients and Net Work	51
4.2	The Carnot Cycle	52
4.3	The Efficiency of Ideal Carnot Engines	54
4.4	Refrigerators and Heat Pumps	56
4.5	The Carnot Cycle and Entropy	58
4.6	The Differential Formulation of Entropy	60
4.7	Entropy Paths	63
4.8	Entropy Changes of the Surroundings	63
4.9	Reversible Paths for Entropy in Irreversible Changes	65
4.10	Non-equilibrium Phase Transitions	65
	Problems	67
5	The Nature of Entropy	71
5.1	The Nature of Entropy	71
5.2	Trouton's Rule	71
5.3	Volume Changes and Randomness	73
5.4	States	73
5.5	States and Probability	74
5.6	Entropy and Temperature	75
5.7	The Entropy of Mixing	76
5.8	Entropy of Mixing for Microscopic States	79
5.9	The Third Law of Thermodynamics	80
5.10	Absolute Entropy Calculations	81
5.11	Residual Entropy	82
5.12	The Gibbs Paradox	83
5.13	Entropy and Information	83
	Problems	86
6	Free Energy	89
6.1	Spontaneity and Entropy	89
6.2	The Free Energies and Work	91
6.3	The Legendre Transform and Thermodynamic Energies	92
6.4	The Mathematical Basis of the Legendre Transform	94
6.5	The Chemical Potential	95
6.6	The Gibbs–Helmholtz Equation	96
6.7	Free Energies and Equilibrium	98
6.8	Fractional Concentrations or Pressures	101
	Problems	104
7	Thermodynamic Equations of State	105
7.1	Maxwell's Relations	105
7.2	Gibbs Free Energy	107
7.3	Other Maxwell's Relations	109
7.4	Adiabatic Demagnetization	110

7.5	The Lippman Equation	111
7.6	Thermodynamic Equations of State	112
7.7	The Joule–Thomson Coefficient	114
	Problems	116
8	Chemical Potentials in Solution	119
8.1	Chemical Potentials for Ideal Solutions	119
8.2	Fugacity	120
8.3	Activity	122
8.4	Partial Molar Quantities	123
8.5	Euler’s theorem	124
8.6	Determining Partial Molar Quantities	125
8.7	The Gibbs–Duhem Equation	125
9	Phase Equilibria and Colligative Properties	129
9.1	Chemical Potential Balance Equations	129
9.2	The Barometric Equation	130
9.3	Sedimentation	131
9.4	Gibbs–Helmholtz Equation and Equilibrium	132
9.5	Osmotic Pressure	133
9.6	Molecular Weight Measurements	135
9.7	The Electrochemical Potential	137
9.8	The Clapeyron Equation	138
9.9	The Clausius–Clapeyron Equation	139
9.10	Freezing Point Depression	140
9.11	Boiling Point Elevation	142
9.12	Donnan Equilibrium	143
	Problems	145
10	The Foundations of Statistical Thermodynamics	149
10.1	The Ergodic Hypothesis	149
10.2	States and Distributions	150
10.3	The Dog-Flea Model	151
10.4	The Most Probable Distribution	153
10.5	Undetermined Multipliers	154
10.6	Energy Distributions	156
10.7	The Boltzmann Factor	158
10.8	Bose–Einstein Statistics	158
10.9	Fermi Dirac Statistics	160
10.10	Other Ensembles	162
	Problems	163
11	Applied Boltzmann Statistics	165
11.1	Boltzmann Statistics for Two-Energy Levels	165
11.2	Unpaired Electrons in a Magnetic Field	166
11.3	The Average Energy	168
11.4	A Differential Expression for Average Energy	170

11.5	Average Entropies and Free Energies	171
11.6	The Chemical Potential	174
11.7	Multi-particle Systems	175
11.8	Energy Manifolds	177
	Problems	178
12	Multi-state Systems	181
12.1	The Harmonic Oscillator	181
12.2	The Classical Limit	183
12.3	The Helmholtz Free Energy and Entropy	184
12.4	Einstein's Crystal Heat Capacity	184
12.5	The Grand and Petit Canonical Partition Functions	186
12.6	Multiple Sites	187
12.7	Binding Averages	188
12.8	A Differential Expression for Average Binding	189
12.9	Macroscopic Equilibria	190
12.10	The Langmuir Adsorption Isotherm	191
12.11	The Brunauer–Emmett Teller (BET) Model	192
	Problems	194
13	Maxwell–Boltzmann Distributions	197
13.1	Distributions for Energy Continua	197
13.2	Useful Integrals	199
13.3	One-Dimensional Velocity Distribution	201
13.4	Mean Square Velocities	203
13.5	Two-Dimensional Distributions	204
13.6	Three-Dimensional Velocity Distributions	205
13.7	The Classical Harmonic Oscillator	209
13.8	The Quantum Rotator	210
13.9	Phase Space	212
13.10	Quantized Phase Space	213
13.11	The Langevin Equation	214
	Problems	215
14	Interactions	217
14.1	A Two-Site Enzyme	217
14.2	Koshland–Nemethy–Filmer Model	217
14.3	Surface Double Layers: Ion Surface Interactions	220
14.4	The Debye–Hückel Theory	223
14.5	One-Dimensional Ising Model	224
14.6	Eigenvalue Techniques	225
14.7	An Eigenvalue Partition Function	226
14.8	The One-Dimensional Ideal Lattice Gas	227
14.9	The Bragg–Williams Approximation	228
	Problems	229

15	Statistical Thermodynamics in Chemical Kinetics	231
15.1	The Dog-Flea Model Revisited	231
15.2	Reversible Reactions and Equilibrium	233
15.3	Kinetic Averages	233
15.4	Stochastic Theory for First-Order Decay	235
15.5	The Wind-Tree Model	237
15.6	The Bimolecular Collision Theory	239
15.7	Transition State Theory	241
15.8	The Energetics of Transition State Theory	242
15.9	Transition State Theory and Partition Functions	243
15.10	The Lindemann Mechanism	245
15.11	Bose–Einstein Statistics	246
15.12	Energy Dependence of k_2	247
15.13	The Continuum Approximation	249
15.14	Energy Transfer	251
	Problems	252
16	Irreversible Thermodynamics and Transport	255
16.1	Charge Flux	255
16.2	Generalized Forces and Fluxes	257
16.3	Particle Flux	259
16.4	Discrete State Membrane Transport	260
16.5	Fick’s Second Law	261
16.6	Discrete State Diffusion	264
16.7	The Nernst Planck Equation	265
16.8	Discrete Diffusion with Drift	268
16.9	Force Coupling	270
16.10	Streaming Current and Electroosmosis	271
16.11	Saxen’s Relations	272
16.12	Scalar Forces and Fluxes	273
	Problems	274
17	Stationary State Thermodynamics	275
17.1	Introduction	275
17.2	Driven System Distributions	278
17.3	General Linearized Driven Systems	280
17.4	The Driven Wind-Tree Model	282
17.5	The Entropy Decrease in Driven Systems	284
17.6	Lasers	286
17.7	The Nerve Impulse	287
17.8	The Prey–Predator Model	289
17.9	Oscillating Reactions	291
17.10	Resonance and Stochastic Resonance	292
17.11	Synchronization	294
	Problem Solutions	297
	Index	309