

Contents

1	Two Fundamental Laws of Nature	1
1.1	Types of Work	1
1.2	The Postulates of Kelvin and Clausius	15
1.3	Carnot's Engine and Temperature	16
1.4	Entropy	22
2	Thermodynamic Functions	27
2.1	Internal Energy and Enthalpy	27
2.2	Simple Applications	29
2.3	Free Energy and Free Enthalpy	54
2.4	Extensive and Intensive Quantities	68
3	Equilibrium and Stability	73
3.1	Equilibrium and Stability via Maximum Entropy	73
3.2	Chemical Potential and Chemical Equilibrium	80
3.3	Applications Involving Chemical Equilibrium	90
4	Simple Phase Diagrams	125
4.1	Van Der Waals Theory	125
4.2	Beyond Van Der Waals Theory	140
4.3	Low Molecular Weight Mixtures	155
4.4	Phase Equilibria in Macromolecular Systems	164
5	Microscopic Interactions	173
5.1	The Canonical Ensemble	173
5.2	Generalized Ensembles	201
5.3	Grand-Canonical Ensemble	205
5.4	The Third Law of Thermodynamics	217
6	Thermodynamics and Molecular Simulation	221
6.1	Metropolis Sampling	221
6.2	Sampling Different Ensembles	225
6.3	Selected Applications	227

7 Non-Equilibrium Thermodynamics 239

7.1 Linear Irreversible Transport 240

7.2 Entropy Production 250

7.3 Complexity in Chemical Reactions 263

7.4 Remarks on Evolution 273

Appendix A: The Mathematics of Thermodynamics 281

Appendix B: Grand-Canonical Monte Carlo:

Methane on Graphite 289

Appendix C: Constants, Units, Tables 293

Index 299