Contents

1 Introduction ............................................................... 1
  Further Reading .......................................................... 2

2 Postulates of Thermodynamics ........................................ 3
  2.1 Thermodynamic Systems: Postulate 1 ............................. 4
    2.1.1 Constrained Systems and the Measurability
    of Energy via Mechanical Work .................................. 6
  2.2 The Conditions of Equilibrium: Postulates 2, 3 and 4 .......... 8
    2.2.1 Properties of the Entropy Function .......................... 10
    2.2.2 Properties of the Differential Fundamental Equation ...... 13
    2.2.3 The Scale of Entropy and Temperature ....................... 15
    2.2.4 Euler Relation, Gibbs–Duhem Equation
    and Equations of State ........................................... 17
    2.2.5 The Fundamental Equation of an Ideal Gas ................. 18
    2.2.6 The Fundamental Equation of an Ideal
    van der Waals Fluid ........................................... 22
  Further Reading ........................................................... 28

3 Thermodynamic Equilibrium in Isolated and Isentropic Systems .... 29
  3.1 Thermal Equilibrium .................................................. 32
  3.2 Thermal and Mechanical Equilibrium .............................. 36
  3.3 Thermal and Chemical Equilibrium ................................ 37
  Further Reading ........................................................... 41

4 Thermodynamic Equilibrium in Systems with Other Constraints .... 43
  4.1 Equilibrium in Constant Pressure Systems:
    The Enthalpy Function ............................................. 44
  4.2 Equilibrium in Constant Temperature and Constant
    Volume Systems: The Free Energy Function ...................... 46
4.3 Equilibrium in Constant Temperature and Constant Pressure Systems: The Gibbs Potential .............................................. 48
4.4 Summary of the Equilibrium Conditions: Properties of the Energy-like Potential Functions ............................................. 50
  4.4.1 Calculation of Heat and Work from Thermodynamic Potential Functions ......................................................... 52
  4.4.2 Calculation of Entropy and Energy-like Functions from Measurable Quantities ................................................. 53
  4.4.3 Calculation of Thermodynamic Quantities from the Fundamental Equation .................................................. 57
4.5 Equations of State of Real Gases, Fluids and Solids .......... 58
  4.5.1 Chemical Potential and Fugacity of a Real Gas .............. 64
Further Reading .................................................................... 68

5 Thermodynamic Processes and Engines ............................. 69
  5.1 Quasistatic, Reversible and Irreversible Processes ............. 69
  5.2 Heat Engines: The Carnot Cycle and the Carnot Engine .......... 72
  5.3 Refrigerators and Heat Pumps: The Carnot Refrigerating and Heat-Pump Cycle .................................................... 75
  5.4 Heat Engines and Refrigerators Used in Practice .............. 77
    5.4.1 Heat Engines Based on the Rankine Cycle ................ 77
    5.4.2 Refrigerators and Heat Pumps Based on the Rankine Cycle ........................................................................ 79
    5.4.3 Isenthalpic Processes: The Joule–Thompson Effect ........ 80
Further Reading .................................................................... 85

6 Thermodynamics of Mixtures (Multicomponent Systems) ......... 87
  6.1 Partial Molar Quantities ............................................. 87
    6.1.1 Chemical Potential as a Partial Molar Quantity .......... 89
    6.1.2 Determination of Partial Molar Quantities from Experimental Data ...................................................... 90
  6.2 Thermodynamics of Ideal Mixtures ................................ 93
    6.2.1 Ideal Gas Mixtures ............................................. 93
    6.2.2 Properties of Ideal Mixtures ................................ 95
    6.2.3 Alternative Reference States ................................. 98
    6.2.4 Activity and Standard State ................................. 101
  6.3 Thermodynamics of Real Mixtures ................................ 103
    6.3.1 Mixtures of Real Gases ...................................... 103
    6.3.2 The Chemical Potential in Terms of Mole Fractions ..... 106
    6.3.3 The Chemical Potential in Terms of Solute Concentration ... 108
    6.3.4 Activity and Standard State: An Overview ............... 109
    6.3.5 Thermodynamic Properties of a Real Mixture ............ 115
  6.4 Ideal Solutions and Ideal Dilute Solutions ....................... 118
Further Reading .................................................................... 122
9.2 Thermodynamic Description of Systems Containing Electrically Charged Particles ...................................... 241

9.2.1 Thermodynamic Consequences of the Electroneutrality Principle: The Chemical Potential of Electrolytes and the Mean Activity Coefficient ......................... 244

9.2.2 Chemical Potential of Ions in an Electric Field: The Electrochemical Potential .................................................. 251

9.2.3 Heterogeneous Electrochemical Equilibria: The Galvanic Cell ............................................................. 253

9.2.4 Electrodes and Electrode Potentials .......................................................... 259

Further Reading ................................................................................. 264

10 Elements of Equilibrium Statistical Thermodynamics .......... 265

10.1 The Microcanonical Ensemble ............................................. 266

10.1.1 Statistical Thermodynamics of the Einstein Solid in Microcanonical Representation ......................................... 269

10.1.2 Statistical Thermodynamics of a System of Two-State Molecules in Microcanonical Representation ........................................ 272

10.2 The Canonical Ensemble ..................................................... 274

10.2.1 Calculation of the Canonical Partition Function from Molecular Data ...................................................... 280

10.2.2 Statistical Thermodynamics of the Einstein Solid and the System of Two-State Molecules in Canonical Representation ...................................... 281

10.2.3 The Translational Partition Function. Statistical Thermodynamics of a Monatomic Ideal Gas ................. 283

10.2.4 Calculation of the Rotational, Vibrational, and Electronic Partition Functions .............................................. 287

10.2.5 Statistical Characterization of the Canonical Energy .... 291

10.2.6 The Equipartition Theorem .................................................. 294

10.3 General Statistical Definition and Interpretation of Entropy .... 297

10.4 Calculation of the Chemical Equilibrium Constant from Canonical Partition Functions ...................................... 300

Further Reading ................................................................................. 306

11 Toward Equilibrium: Elements of Transport Phenomena ....... 307

11.1 Transport Equations for Heat, Electricity, and Momentum ...... 309

11.2 Equations for the Diffusive Material Transport ..................... 311

11.2.1 Fick’s First Law: The Flux of Diffusion ............................... 312

11.2.2 Fick’s Second Law: The Rate of Change of the Concentration Profile ......................................... 312

11.3 Principle Transport Processes and Coupled Processes .......... 316

Further Reading ................................................................................. 318
Appendix  ......................................................................................................................... 319
A1 Useful Relations of Multivariate Calculus ............................................. 319
   A.1.1 Differentiation of Multivariate Functions .............................. 319
   A.1.2 Differentiation of Composite Functions ......................... 322
   A.1.3 Differentiation of Implicit Functions ................................. 323
   A.1.4 Integration of Multivariate Functions .............................. 324
   A.1.5 The Euler Equation for Homogeneous
       First-Order Functions .................................................. 325
A2 Changing Extensive Variables to Intensive Ones:
   Legendre Transformation .............................................................. 326
   A.2.1 Legendre Transformations ........................................... 327
   A.2.2 Legendre Transformation of the Entropy Function ............. 329
A3 Classical Thermodynamics: The Laws ............................................. 331
   A.3.1 Zeroth Law and Temperature ......................................... 332
   A.3.2 First Law and Energy .................................................. 334
   A.3.3 Second Law and Entropy ............................................... 336
   A.3.4 Third Law and the Uniqueness of the Entropy Scale ......... 341
Further Reading ................................................................................................. 341

Index ......................................................................................................................... 343