

TABLE OF CONTENTS

Licensing

About the Author

1: Introduction - Background and a Look Ahead

- 1.1: The Role of the Ideal Gas
- 1.2: Chemical Kinetics
- 1.3: Classical Thermodynamics
- 1.4: Statistical Thermodynamics
- 1.5: Heat Transfer in Practical Devices
- 1.6: The Concept of Equilibrium
- 1.7: Chemical Equilibrium and Predicting Chemical Change
- 1.8: Equilibrium and Classical Thermodynamics
- 1.9: A Few Ideas from the Philosophy of Science
- 1.10: A Few Ideas from Formal Logic
- 1.11: Problems

2: Gas Laws

- 2.1: Boyle's Law
- 2.2: Charles' Law
- 2.3: Avogadro's Hypothesis
- 2.4: Finding Avogadro's Number
- 2.5: The Kelvin Temperature Scale
- 2.6: Deriving the Ideal Gas Law from Boyle's and Charles' Laws
- 2.7: The Ideal Gas Constant and Boltzmann's Constant
- 2.8: Real Gases Versus Ideal Gases
- 2.9: Temperature and the Ideal Gas Thermometer
- 2.10: Deriving Boyle's Law from Newtonian Mechanics
- 2.11: The Barometric Formula
- 2.12: Van der Waals' Equation
- 2.13: Virial Equations
- 2.14: Gas Mixtures - Dalton's Law of Partial Pressures
- 2.15: Gas Mixtures - Amagat's Law of Partial Volumes
- 2.16: Problems

3: Distributions, Probability, and Expected Values

- 3.1: The Distribution Function as a Summary of Experimental Results
- 3.2: Outcomes, Events, and Probability
- 3.3: Some Important Properties of Events
- 3.4: Applying the Laws of Probability
- 3.5: Bar Graphs and Histograms
- 3.6: Continuous Distribution Functions - the Envelope Function is the Derivative of the Area
- 3.7: A Heuristic View of the Probability Density Function
- 3.8: A Heuristic View of the Cumulative Distribution Function
- 3.9: Random Variables, Expected Values, and Population Sets
- 3.10: Statistics - the Mean and the Variance of a Distribution
- 3.11: The Variance of the Average- The Central Limit Theorem

- 3.12: The Normal Distribution
- 3.13: The Expected Value of a Function of Several Variables and the Central Limit Theorem
- 3.14: Where Does the $N - 1$ Come from?
- 3.15: Problems

4: The Distribution of Gas Velocities

- 4.1: Distribution Functions for Gas-velocity Components
- 4.2: Probability Density Functions for Velocity Components in Spherical Coordinates
- 4.3: Maxwell's Derivation of the Gas-velocity Probability-density Function
- 4.4: The Probability-density Function for Gas Velocities in One Dimension
- 4.5: Combining the One-dimensional Probability Density Functions
- 4.6: Boyle's Law from the Maxwell-Boltzmann Probability Density
- 4.7: Experimental Test of the Maxwell-Boltzmann Probability Density
- 4.8: Statistics for Molecular Speeds
- 4.9: Pressure Variations for Macroscopic Samples
- 4.10: Collisions between Gas Molecules Relative Velocity Coordinates
- 4.11: The Probability Density Function for the Relative Velocity
- 4.12: The Frequency of Collisions between Unlike Gas Molecules
- 4.13: The Rate of Collisions between Unlike Gas Molecules
- 4.14: Collisions between like Gas Molecules
- 4.15: The Geometry of A Collision between Spherical Molecules
- 4.16: The Energy of A Collision between Gas Molecules
- 4.17: Problems

5: Chemical Kinetics, Reaction Mechanisms, and Chemical Equilibrium

- 5.1: Chemical Kinetics
- 5.2: Reaction Rates and Rate Laws
- 5.3: Simultaneous Processes
- 5.4: The Effect of Temperature on Reaction Rates
- 5.5: Other Factors that Affect Reaction Rates
- 5.6: Mechanisms and Elementary Processes
- 5.7: Rate Laws for Elementary Processes
- 5.8: Experimental Determination of Rate Laws
- 5.9: First-order Rate Processes
- 5.10: Rate Laws by the Study of Initial Rates
- 5.11: Rate Laws from Experiments in a Continuous Stirred Tank Reactor
- 5.12: Predicting Rate Laws from Proposed Mechanisms
- 5.13: The Michaelis-Menten Mechanism for Enzyme-catalyzed Reactions
- 5.14: The Lindemann-Hinshelwood Mechanism for First-order Decay
- 5.15: Why Unimolecular Reactions are First Order
- 5.16: The Mechanism of the Base Hydrolysis of $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$
- 5.17: Chemical Equilibrium as the Equality of Rates for Opposing Reactions
- 5.18: The Principle of Microscopic Reversibility
- 5.19: Microscopic Reversibility and the Second Law
- 5.20: Problems

6: Equilibrium States and Reversible Processes

- 6.1: The Thermodynamic Perspective
- 6.2: Thermodynamic Systems and Variables
- 6.3: Equilibrium and Reversibility - Phase Equilibria
- 6.4: Distribution Equilibria

- 6.5: Equilibria in Chemical Reactions
- 6.6: Le Chatelier's Principle
- 6.7: The Number of Variables Required to Specify Some Familiar Systems
- 6.8: Gibbs' Phase Rule
- 6.9: Reversible vs. Irreversible Processes
- 6.10: Duhem's Theorem - Specifying Reversible Change in A Closed System
- 6.11: Reversible Motion of A Mass in A Constant Gravitational Field
- 6.12: Equilibria and Reversible Processes
- 6.13: The Laws of Thermodynamics
- 6.14: Thermodynamic Criteria for Change
- 6.15: State Functions in Systems Undergoing Spontaneous Change
- 6.16: Problems

7: State Functions and The First Law

- 7.1: Changes in a State Function are Independent of Path
- 7.2: The Total Differential
- 7.3: Line Integrals
- 7.4: Exact Differentials and State Functions
- 7.5: Determining Whether an Expression is an Exact Differential
- 7.6: The Chain Rule and the Divide-through Rule
- 7.7: Measuring Pressure-Volume Work
- 7.8: Measuring Work- Non-Pressure-Volume Work
- 7.9: Measuring Heat
- 7.10: The First Law of Thermodynamics
- 7.11: Other Statements of the First Law
- 7.12: Notation for Changes in Thermodynamic Quantities - E vs. ΔE
- 7.13: Heat Capacities for Gases- C_v , C_p
- 7.14: Heat Capacities of Solids- the Law of Dulong and Petit
- 7.15: Defining Enthalpy, H
- 7.16: Heat Transfer in Reversible Processes
- 7.17: Free Expansion of a Gas
- 7.18: Reversible vs. Irreversible Pressure-Volume Work
- 7.19: Isothermal Expansions of An Ideal Gas
- 7.20: Adiabatic Expansions of An Ideal Gas
- 7.21: Problems

8: Enthalpy and Thermochemical Cycles

- 8.1: Enthalpy
- 8.2: Using Thermochemical Cycles to Find Enthalpy Changes
- 8.3: How Enthalpy Depends on Pressure
- 8.4: Standard States and Enthalpies of Formation
- 8.5: The Ideal Gas Standard State
- 8.6: Standard Enthalpies of Reaction
- 8.7: Standard State Heat Capacities
- 8.8: How The Enthalpy Change for a Reaction Depends on Temperature
- 8.9: Calorimetry
- 8.10: Problems

9: The Second Law - Entropy and Spontaneous Change

- 9.1: The Second Law of Thermodynamics
- 9.2: The Carnot Cycle for an Ideal Gas and the Entropy Concept

- 9.3: The Carnot Cycle for Any Reversible System
- 9.4: The Entropy Change around Any Cycle for Any Reversible System
- 9.5: The Tiling Theorem and the Paths of Cyclic Process in Other Spaces
- 9.6: Entropy Changes for A Reversible Process
- 9.7: Entropy Changes for A Spontaneous Process in An Isolated System
- 9.8: The Entropy of the Universe
- 9.9: The Significance of The Machine-based Statement of The Second Law
- 9.10: A Slightly Philosophical Digression on Energy and Entropy
- 9.11: A Third Statement of the Second Law
- 9.12: Entropy and Predicting Change
- 9.13: Defining the Helmholtz and Gibbs Free Energies
- 9.14: The Fundamental Equation and Other Criteria for Reversible Change
- 9.15: Entropy and Spontaneous Change
- 9.16: Internal Entropy and the Second Law
- 9.17: Notation and Terminology- Conventions for Spontaneous Processes
- 9.18: The Heat Exchanged by A Spontaneous Process at Constant Entropy
- 9.19: The Energy Change for A Spontaneous Process at Constant S and V
- 9.20: The Enthalpy Change for A Spontaneous Process at Constant S and P
- 9.21: The Entropy Change for A Spontaneous Process at Constant E and V
- 9.22: The Entropy Change for A Spontaneous Process at Constant H and P
- 9.23: The Reversible Work is the Minimum Work at Constant T^*
- 9.24: The Free Energy Changes for A Spontaneous Process at Constant T^*
- 9.25: Summary- Thermodynamic Functions as Criteria for Change
- 9.26: Problems

10: Some Mathematical Consequences of the Fundamental Equation

- 10.1: Thermodynamic Relationships from dE , dH , dA and dG
- 10.2: $dE = TdS - PdV$ and Internal consistency
- 10.3: Expressing Thermodynamic Functions with Other Independent Variables
- 10.4: Expressing Thermodynamic Functions with Independent Variables V and T
- 10.5: Expressing Thermodynamic Functions with Independent Variables P and T
- 10.6: The Transformation of Thermodynamic Variables in General
- 10.7: Reversibility and Thermodynamic Variables in General
- 10.8: Using the Pair (V, P) or the Pair (T, S) as Independent Variables
- 10.9: The Relationship Between C_v and C_p for Any Substance
- 10.10: The Dependence of C_v on Volume and of C_p on Pressure
- 10.11: The Gibbs-Helmholtz Equation
- 10.12: The Second Law and the Properties of Ideal Gases
- 10.13: The second-dependence of the Energy and Enthalpy of A Real Gas
- 10.14: The Joule-Thomson Effect
- 10.15: Problems

11: The Third Law, Absolute Entropy, and the Gibbs Free Energy of Formation

- 11.1: Heat Capacity as a Function of Temperature
- 11.2: Enthalpy as a function of Temperature
- 11.3: The Third Law
- 11.4: Genesis of the Third Law - the Nernst Heat Theorem
- 11.5: Absolute Entropy
- 11.6: The Standard State for Third-law Entropies
- 11.7: The Fugacity of a Gas

- 11.8: A General Strategy for Expressing the Thermodynamic Properties of a Substance
- 11.9: The Standard Entropy and the Gibbs Free Energy of Formation
- 11.10: The Nature of Hypothetical States
- 11.11: The Fugacity and Gibbs Free Energy of A Substance in Any System
- 11.12: Evaluating Entropy Changes Using Thermochemical Cycles
- 11.13: Absolute Zero is Unattainable
- 11.14: Problems

12: Applications of the Thermodynamic Criteria for Change

- 12.1: Mechanical Processes
- 12.2: The Direction of Spontaneous Heat Transfer
- 12.3: Phase Changes - the Fusion of Ice
- 12.4: Measuring the Entropy Change for Any Reversible Process
- 12.5: Another Perspective on the Principle of Le Chatelier
- 12.6: Phase Equilibria - Temperature Dependence of the Boiling Point
- 12.7: Phase Equilibria - Temperature Dependence of the Melting Point
- 12.8: The Clapeyron Equation
- 12.9: The Clausius-Clapeyron Equation
- 12.10: Problems

13: Equilibria in Reactions of Ideal Gases

- 13.1: The Gibbs Free Energy of an Ideal Gas
- 13.2: The Gibbs Free Energy Change for A Reaction of Ideal Gases
- 13.3: The Thermodynamics of Mixing Ideal Gases
- 13.4: The Gibbs Free Energy Change for Reaction at Constant Partial Pressures
- 13.5: $\Delta_r G$ is the rate at which the Gibbs Free Energy Changes with The Extent of Reaction
- 13.6: The Standard Gibbs Free Energy Change and Equilibrium in Ideal Gas Reactions
- 13.7: The Gibbs Free Energy of Formation and Equilibrium in Ideal Gas Reactions
- 13.8: Equilibrium When A Component is Also Present as A Condensed Phase
- 13.9: Equilibrium When An Ideal Gas Component is Also Present as A solute
- 13.10: Problems

14: Chemical Potential - Extending the Scope of the Fundamental Equation

- 14.1: Dependence of the Internal Energy on the Composition of the System
- 14.2: Dependence of Other Thermodynamic Functions on the Composition
- 14.3: Partial Molar Quantities
- 14.4: Chemical Potentials and Stoichiometry
- 14.5: $\sum \mu_j dn_j = 0$ and Primitive Vs. Gibbsian Equilibrium
- 14.6: The Change Criteria in A System Composed of Subsystems
- 14.7: At Constant P and T, $\Delta_r \mu$ is the Change in Gibbs Free Energy
- 14.8: Gibbs-Duhem Equation
- 14.9: The Dependence of Chemical Potential on Other Variables
- 14.10: Chemical Activity
- 14.11: Back to the Fugacity- the Fugacity of A Component of A Gas Mixture
- 14.12: Relating Fugacity and Chemical Activity
- 14.13: Relating the Differentials of Chemical Potential and Activity
- 14.14: Dependence of Activity on Temperature- Relative Partial Molar Enthalpies
- 14.15: Problems

15: Chemical Potential, Fugacity, Activity, and Equilibrium

- 15.1: The Chemical Potential and Fugacity of a Gas
- 15.2: The Chemical Potential and Activity of a Gas
- 15.3: The Pressure-dependence of the Fugacity and Activity of a Condensed Phase
- 15.4: Standard States for the Fugacity and Activity of a Pure Solid
- 15.5: The Chemical Potential, Fugacity, and Activity of a Pure Solid
- 15.6: Chemical Potential, Fugacity, and Equilibrium
- 15.7: Chemical Potential, Activity, and Equilibrium
- 15.8: The Rate of Gibbs Free Energy Change with Extent of Reaction
- 15.9: Problems

16: The Chemical Activity of the Components of a Solution

- 16.1: Solutions Whose Components are in Equilibrium with Their Own Gases
- 16.2: Raoult's Law and Ideal Solutions
- 16.3: Expressing the Activity Coefficient as a Deviation from Raoult's Law
- 16.4: Henry's Law and the Fugacity and Activity of A Solution Component
- 16.5: Expressing the Activity Coefficient as A Deviation from Henry's Law
- 16.6: Henry's Law and the Hypothetical One-molal Standard State
- 16.7: Finding the Activity of a Solute from the Activity of the Solvent
- 16.8: When the Solute Obeys Henry's Law, the Solvent Obeys Raoult's Law
- 16.9: Properties of Ideal Solutions
- 16.10: Colligative Properties - Boiling-point Elevation
- 16.11: Colligative Properties - Freezing-point Depression
- 16.12: Colligative Properties - Osmotic Pressure
- 16.13: Colligative Properties - Solubility of a Solute in an Ideal Solution
- 16.14: Colligative Properties - Solubility of a Gas
- 16.15: Solvent Activity Coefficients from Freezing-point Depression Measurements
- 16.16: Electrolytic Solutions
- 16.17: Activities of Electrolytes - The Mean Activity Coefficient
- 16.18: Activities of Electrolytes - The Debye-Hückel Theory
- 16.19: Finding Solute Activity Using the Hypothetical One-molal Standard State
- 16.20: Problems

17: Electrochemistry

- 17.1: Oxidation-reduction Reactions
- 17.2: Electrochemical Cells
- 17.3: Defining Oxidation States
- 17.4: Balancing Oxidation-reduction Reactions
- 17.5: Electrical Potential
- 17.6: Electrochemical Cells as Circuit Elements
- 17.7: The Direction of Electron Flow and its Implications
- 17.8: Electrolysis and the Faraday
- 17.9: Electrochemistry and Conductivity
- 17.10: The Standard Hydrogen Electrode (S.H.E)
- 17.11: Half-reactions and Half-cells
- 17.12: Standard Electrode Potentials
- 17.13: Predicting the Direction of Spontaneous Change
- 17.14: Cell Potentials and the Gibbs Free Energy
- 17.15: The Nernst Equation
- 17.16: The Nernst Equation for Half-cells
- 17.17: Combining two Half-cell Equations to Obtain a new Half-cell Equation

- 17.18: The Nernst Equation and the Criterion for Equilibrium
- 17.19: Problems

18: Quantum Mechanics and Molecular Energy Levels

- 18.1: Energy Distributions and Energy Levels
- 18.2: Quantized Energy - De Broglie's Hypothesis and the Schroedinger Equation
- 18.3: The Schrödinger Equation for A Particle in A Box
- 18.4: The Schrödinger Equation for a Molecule
- 18.5: Solutions to Schroedinger Equations for Harmonic Oscillators and Rigid Rotors
- 18.6: Wave Functions, Quantum States, Energy Levels, and Degeneracies
- 18.7: Particle Spins and Statistics- Bose-Einstein and Fermi-Dirac Statistics

19: The Distribution of Outcomes for Multiple Trials

- 19.1: Distribution of Results for Multiple Trials with Two Possible Outcomes
- 19.2: Distribution of Results for Multiple Trials with Three Possible Outcomes
- 19.3: Distribution of Results for Multiple Trials with Many Possible Outcomes
- 19.4: Stirling's Approximation
- 19.5: Problems

20: Boltzmann Statistics

- 20.1: The Independent-Molecule Approximation
- 20.2: The Probability of An Energy Level at Constant N, V, and T
- 20.3: The Population Sets of a System at Equilibrium at Constant N, V, and T
- 20.4: How can Infinitely Many Probabilities Sum to Unity?
- 20.5: The Total Probability Sum at Constant N, V, and T
- 20.6: The Most Probable Population Set at Constant N, V, and T
- 20.7: The Microstates of a Given Population Set
- 20.8: The Probabilities of Microstates that Have the Same Energy
- 20.9: The Probabilities of the Population Sets of an Isolated System
- 20.10: Entropy and Equilibrium in an Isolated System
- 20.11: Thermodynamic Probability and Equilibrium in an Isomerization Reaction
- 20.12: The Degeneracy of an Isolated System and Its Entropy
- 20.13: The Degeneracy of an Isolated System and its Entropy
- 20.14: Effective Equivalence of the Isothermal and Constant-energy Conditions
- 20.15: Problems

21: The Boltzmann Distribution Function

- 21.1: Finding the Boltzmann Equation
- 21.2: Lagrange's Method of Undetermined Multipliers
- 21.3: Deriving the Boltzmann Equation I
- 21.4: Deriving the Boltzmann Equation II
- 21.5: Partition Functions and Equilibrium - Isomeric Molecules
- 21.6: Finding β and the Thermodynamic Functions for Distinguishable Molecules
- 21.7: The Microscopic Model for Reversible Change
- 21.8: The Third Law of Thermodynamics
- 21.9: The Partition Function for a System of N Molecules
- 21.10: Problems

22: Some Basic Applications of Statistical Thermodynamics

- 22.1: Interpreting the Partition Function
- 22.2: Conditions under which Integrals Approximate Partition Functions
- 22.3: Probability Density Functions from the Energies of Classical-mechanical Models
- 22.4: Partition Functions and Average Energies at High Temperatures
- 22.5: Energy Levels for a Three-dimensional Harmonic Oscillator
- 22.6: Energy and Heat Capacity of the "Einstein Crystal"
- 22.7: Applications of Other Entropy Relationships
- 22.8: Problems

23: The Ensemble Treatment

- 23.1: Ensembles of N-molecule Systems
- 23.2: The Ensemble Entropy and the Value of β
- 23.3: The Thermodynamic Functions of the N-molecule System

24: Indistinguishable Molecules - Statistical Thermodynamics of Ideal Gases

- 24.1: The Partition Function for N Distinguishable, Non-interacting Molecules
- 24.2: The Partition Function for N Indistinguishable, Non-interacting Molecules
- 24.3: Occupancy Probabilities for Translational Energy Levels
- 24.4: The Separable-modes molecular Model
- 24.5: The Partition Function for A Gas of Indistinguishable, Non-interacting, Separable-modes Molecules
- 24.6: The Translational Partition Function of An Ideal Gas
- 24.7: The Electronic Partition Function of an Ideal Gas
- 24.8: The Vibrational Partition Function of A Diatomic Ideal Gas
- 24.9: The Rotational Partition Function of A Diatomic Ideal Gas
- 24.10: The Gibbs Free Energy for One Mole of An Ideal Gas
- 24.11: The Standard Gibbs Free Energy for $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$
- 24.12: The Gibbs Free Energy Change for Forming $\text{HI}(\text{g})$ from $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$
- 24.13: The Reference State for Molecular Partition Functions
- 24.14: Problems

25: Bose-Einstein and Fermi-Dirac Statistics

- 25.1: Quantum Statistics
- 25.2: Fermi-Dirac Statistics and the Fermi-Dirac Distribution Function
- 25.3: Bose-Einstein Statistics and the Bose-Einstein Distribution Function

26: Appendices

- 26.1: Appendix A. Standard Atomic Weights 1999†
- 26.2: Appendix B.
- 26.3: Appendix B. Fundamental Constants†
- 26.4: Appendix C.
- 26.5: Units and Conversion Factors
- 26.6: Appendix D.
- 26.7: Appendix D. Some Important Definite Integrals

Index

[Index](#)

[Glossary](#)

[Detailed Licensing](#)