Contents

Preface v

1. Scope of Thermodynamics 1

   1.1 The verdict on thermodynamics 2
   1.2 The need for a macroscopic description 3
      1.2.1 Ideal gas: A macroscopic description 4
      1.2.2 Measurement of temperature 6
      1.2.3 Ideal gas: A microscopic description 11
   1.3 What will thermodynamics do for you? 15
   1.4 What does thermodynamics not do for you? 15
   1.5 Problems 16

2. The Structure of Thermodynamics 19

   2.1 Large systems 19
   2.2 Macroscopic variables 20
      2.2.1 Equilibrium: A question of time and history . . . 20
      2.2.2 The fundamental relation: Entropy 22
   2.3 Measurement and walls 24
      2.3.1 Walls 24
      2.3.2 Energy measurement 25
   2.4 Problems 33

3. The Laws of Thermodynamics 37

   3.1 Zeroth law: The fundamental relation 37
   3.2 First law: Energy conservation 38
   3.3 Second law: Entropy always rises 42

THERMODYNAMICS
© World Scientific Publishing Co. Pte. Ltd.
http://www.worldscibooks.com/physics/7964.html

3.3.1 Examples of the second law in physical systems . 43
3.4 Understanding the second law 44
3.5 Consequences of the first and second laws 47
3.6 Third law or Nernst's theorem: Zero temperature cannot be attained 50
3.7 Problems 52

4. Intensive Variables 55

4.1 Pressure 56
4.2 Temperature 57
4.3 Chemical potentials 57
4.4 Intensive variables in the entropy representation 58
4.5 More on the physical significance of intensive variables . . 62
4.6 Euler equation and Gibbs-Duhem relation 64
4.7 Problems 65

5. Simple Systems 69

5.1 Second derivatives: expansion coefficient, compressibility, heat capacity, and more 69
5.2 Mixture of ideal gases 71
5.3 Gas reactions 76
5.4 Blackbody radiation 79
5.5 Polymers 81
5.6 Thermodynamics of adsorbates 85
5.7 Magnetic systems 93
5.7.1 Diamagnetism 93
5.7.2 Paramagnetism 95
5.7.3 Ferromagnetism 96
5.7.4 Fundamental relation for magnetic systems 98
5.8 Problems 99

6. Thermodynamic Potentials 103

6.1 Introducing internal constraints via reservoirs 104
6.2 Helmholtz free energy 107
6.3 Enthalpy 109
6.3.1 Joule-Thomson "throttling" process 110
6.3.2 Gas liquefaction 113
6.4 Gibbs free energy 115

THERMODYNAMICS
© World Scientific Publishing Co. Pte. Ltd.
http://www.worldscibooks.com/physics/7964.html

6.4.1 Vapor pressure of small droplets 116
6.4.2 Osmosis 118
6.5 Problems 121

7. Maxwell Relations 123

7.1 Maxwell relations 123
7.2 Reduction of derivatives 126
7.3 Applications 129
7.3.1 Adiabatic compression 129
7.3.2 Isothermal compression 131
7.3.3 Free expansion 132
7.3.4 Joule-Thomson throttling process 133
7.3.5 Heating a room 135
7.4 Problems 138

8. Engines, Hurricanes, and Athletes 141

8.1 The Carnot cycle 142
8.2 Maximum work theorem 144
8.3 Engine efficiency 147
8.3.1 Gasoline engine: the Otto cycle 147
8.3.2 Diesel engine 149
8.3.3 Otto versus Diesel 151
8.3.4 Refrigerator 153
8.3.5 Heat pump 154
8.4 Cyclones 155
8.4.1 The greenhouse effect 156
8.4.2 A Carnot engine 157
8.5 Athletes: the human engine 160
8.6 Thermodynamics in economics 162
8.7 Problems 166

9. Stability of Thermodynamic Systems 169

9.1 Macroscopic motion 169
9.2 Thermodynamic inequalities 171
9.3 Fluctuations and the principle of Le Chatelier and Braun 173

10. Phase Transitions 177

THERMODYNAMICS
© World Scientific Publishing Co. Pte. Ltd.
http://www.worldscibooks.com/physics/7964.html

10.1 Latent heat 182
10.2 Clausius-Clapeyron equation 185
10.3 Van der Waals gas 187
10.4 Metastability: supersaturated water and overheated liquid 193
10.5 The critical point 196
10.6 The law of corresponding states and universality 199
10.7 Landau theory of phase transitions 201
10.8 No phase transitions in one-dimensional systems (almost) 203
10.9 Problems 206

11. Summary of Useful Results and Final Remarks 209

11.1 Thermodynamic potentials 209
11.1.1 Entropy $S(U, V, N)$ 209
11.1.2 Internal energy and others 209
11.2 Ideal gas 210
11.3 Van der Waals gas 211
11.4 Polymers 212
11.5 Joule-Thomson throttling 212
11.6 Engines 212
11.7 Phase transitions 213
11.8 Final remarks: beyond equilibrium thermodynamics . . . 213

Appendix A Partial Derivatives and Differential Forms 217

Bibliography 221

Index 223

THERMODYNAMICS
© World Scientific Publishing Co. Pte. Ltd.
http://www.worldscibooks.com/physics/7964.html