

## Contents

(Sections marked with an asterisk may be omitted at first reading.)

<i>Preface</i>	xiii
<b>1 Introduction: thermodynamic systems seen from outside</b>	<b>1</b>
1.1 Background ideas	1
1.2 The approach to thermodynamics through statistical mechanics	2
1.3 The thermodynamic state	3
1.4 Energy in thermodynamic systems	6
1.5 Empirical temperature	8
1.6 The tasks of a mechanistic theory	9
<b>2 The statistical foundations</b>	<b>11</b>
2.1 Probability	11
2.2 Manipulations involving probability	13
2.3 Quantum states and their distribution in energy	14
2.4 Quantum jump rates and the master equation	17
2.5 The ergodic assumption	21
2.6 The principle of equal equilibrium probability	22
*2.7 The principle of detailed balance	23
<b>3 Temperature</b>	<b>25</b>
3.1 The meaning of temperature for large systems	25
3.2 Thermal equilibrium between two large systems	29
3.3 Boltzmann's distribution and the meaning of temperature for small systems	30
*3.4 The energy distribution for a large system at a given temperature	33
*3.5 Can heat capacity or temperature be negative?	35
Problems	37
<b>4 Entropy</b>	<b>38</b>
4.1 The Boltzmann–Gibbs statistical picture of entropy	38
4.2 The law of increase of entropy	39
4.3 The equilibrium entropy	40
4.4 The connection between equilibrium entropy and reversible heat and work	43

viii	<i>Contents</i>	
*4.5	The third law	44
	Problems	46
<b>5</b>	<b>Elementary theory of the ideal monatomic gas</b>	<b>47</b>
5.1	The model of the gas	47
5.2	The one-component velocity distribution and the internal energy	49
5.3	The speed distribution	50
5.4	The equation of state	51
5.5	Gas scale temperature, the energy $kT$ and Boltzmann's constant	52
5.6	Properties related to heat entering the gas	54
	Problems	55
<b>6</b>	<b>The basic principles of classical thermodynamics</b>	<b>56</b>
6.1	General assumptions	56
6.2	The first law	57
6.3	The second law: entropy	57
6.4	The second law: temperature	58
6.5	The second law: heat engines	59
6.6	Thermodynamic and gas scale temperatures	61
6.7	The relation between pressure and entropy	63
6.8	The general expression for $dE$ in terms of state functions	64
6.9	Entropy, heat and the third law	65
	Problems	66
<b>7</b>	<b>Energies in classical thermodynamics</b>	<b>67</b>
7.1	Thermodynamic potentials	67
7.2	Potential energy in thermodynamic systems: free energy	68
7.3	Energy in flow processes: enthalpy	72
7.4	Energy in phase changes and chemical reactions: enthalpy and Gibbs function	74
7.5	Useful work and the general condition for equilibrium: availability	74
	Problems	76
<b>8</b>	<b>Thermodynamic relations</b>	<b>78</b>
8.1	Partial derivatives	78
8.2	Maxwell relations	79
8.3	Examples of thermodynamic relations	80
8.3.1	Vapour pressure and latent heat	80
8.3.2	Relations involving $C_p$ and $C_v$	81
8.3.3	Expansion coefficients at low temperatures	82
8.3.4	The energy density of equilibrium radiation	82
8.3.5	Heats of reaction from cell voltages	83
	Problems	84
<b>9</b>	<b>Statistical calculation of thermodynamic quantities</b>	<b>86</b>
9.1	First method: direct application of the Boltzmann distribution	86

<i>Contents</i>	ix
9.1.1 Energy and entropy of a harmonic oscillator	87
9.1.2 Energy of vibration and rotation in an asymmetrical diatomic gas	89
9.1.3 Pressure of electromagnetic radiation	91
9.2 Second method: calculation of the free energy from the partition function	93
9.2.1 Magnetisation and entropy of a paramagnetic salt with $S = \frac{1}{2}$	94
9.3 Third method: calculation of the entropy as $k \ln g$ or $k \ln W$ for large systems	96
9.3.1 The equilibrium concentration of vacancies in a solid	98
Problems	100
<b>10 Waves in a box</b>	<b>102</b>
10.1 The density of modes in $k$ space	102
10.2 The spectral distribution for temperature radiation	103
10.3 Absorption and emission	106
10.4 Lattice heat capacity of a solid	107
Problems	111
<b>11 Systems with variable contents</b>	<b>113</b>
11.1 Semi-permeable membrane and particle reservoir	113
11.2 Chemical potential	114
11.3 Energy relations involving the chemical potential	115
11.4 The Gibbs distribution	117
Problems	118
<b>12 Indistinguishable particles</b>	<b>120</b>
12.1 Identifiable system and indistinguishable particle	120
12.2 Bosons and Fermions	122
12.3 The Bose–Einstein and Fermi–Dirac distributions	124
12.4 Properties of the Fermi–Dirac distribution	126
12.5 The variation of $\mu$ with $T$ at fixed density	129
12.6 Non-condensed gases	131
12.7 The law of mass action	134
12.8 Entropy of mixing	136
Problems	137
<b>13 Classical statistical mechanics</b>	<b>139</b>
13.1 The classical limit of quantum theory	139
13.2 The phase space picture of the approach to equilibrium	144
13.3 Liouville’s theorem	145
13.4 The fundamental results in the classical formulation	147
13.5 The classical equipartition theorem	149
Problems	152
<b>14 The problem of the equation of state</b>	<b>153</b>
14.1 Intermolecular forces	153
14.2 The virial theorem	155
14.3 The second virial coefficient	158

x	<i>Contents</i>	
	14.4 The physical behaviour of imperfect gases	159
	*14.5 The virial expansion	162
	*14.6 Attempts to analyse the high density limit	165
	14.7 The law of corresponding states	167
	14.8 Direct computation for small numbers of molecules	170
	14.9 The hard sphere fluid	173
	14.10 The modified hard sphere fluid	175
	14.11 Summary	179
	Problems	179
	<b>15 Electric and magnetic systems</b>	<b>181</b>
	15.1 Electrical energy and electrical work	181
	15.2 Magnetic energy and magnetic work	183
	15.3 Spin systems	185
	15.4 Cooling by adiabatic demagnetisation	186
	15.5 The superconducting critical field	190
	15.6 The electrochemical potential	194
	Problems	197
	<b>16 Fluctuations and the approach to equilibrium</b>	<b>199</b>
	16.1 The equilibrium distribution of fluctuations: general principles	199
	*16.2 Special difficulties in certain cases	200
	16.3 Example: fluctuations of magnetisation in a simple paramagnetic salt	202
	16.4 Relations between fluctuations and thermodynamic response functions	203
	16.5 The power spectrum of thermal fluctuations	209
	16.6 Thermally activated processes	213
	16.7 The dependence of scattering rates on occupation numbers	218
	Problems	221
	<b>17 Transport properties</b>	<b>223</b>
	17.1 The mean free path method	224
	17.2 Relaxation time approximations	227
	17.3 The Boltzmann transport equation	229
	17.4 Transport properties of metals	231
	17.4.1 The electrical conductivity	233
	17.4.2 The thermopower	234
	17.4.3 Thermal conductivity and the Wiedemann–Franz law	235
	17.5 Thermoelectric heat flows and the Thomson relations	236
	17.6 Non-equilibrium thermodynamics applied to thermoelectricity	238
	*17.7 Onsager’s proof of the reciprocal relations	241
	Problems	244
	<b>18 Phase transitions</b>	<b>246</b>
	18.1 Phenomena	246
	18.2 The Weiss model of ferromagnetism in zero applied field	251

<i>Contents</i>	xi
18.3 The Weiss model in an applied field	254
18.4 van der Waals' model of the liquid–vapour transition	257
18.5 The mixed phase region	258
18.6 The nucleation barrier and metastability	263
*18.7 The rate of phase nucleation	265
18.8 Phase transitions in systems of two or more species	268
18.9 Critical exponents and the scaling hypothesis	275
*18.10 Theories of critical point behaviour	280
Problems	285
<b>19 The fundamental assumptions reviewed</b>	<b>288</b>
19.1 Accessibility and the ergodic assumption	288
19.2 The problem of time reversal symmetry	292
19.3 Coarse graining and the classical <i>H</i> -theorem	297
19.4 Matrix mechanics and the density matrix	298
19.5 The equilibrium density matrix	301
19.6 The approach to equilibrium in quantum theory	302
19.7 The behaviour of entropy during fluctuations	306
<i>Answers to problems</i>	309
<i>Suggestions for further reading</i>	313
<i>References</i>	316
<i>Index and table of symbols</i>	319
<i>Table of constants</i>	336