## Contents

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

	Preface	xiii
1	Introduction: thermodynamic systems seen from outside	1
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
2	The statistical foundations	11
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
3	Temperature	25
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
4	Entropy	38
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	Contents

4.5	The third law . Problems	44 46
5	Elementary theory of the ideal monatomic gas	47
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	52
	Boltzmann's constant	
5.6	Properties related to heat entering the gas	54
	Problems	55
6	The basic principles of classical thermodynamics	56
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
0.5	Problems	66
7	Energies in classical thermodynamics	67
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:	74
	enthalpy and Gibbs function	
7.5		74
	availability	
	Problems	76
8	Thermodynamic relations	78
8.1	Partial derivatives	78
8.2	Maxwell relations	79
8.3	Examples of thermodynamic relations	80
8.3.1		80
8.3.2	Relations involving $C_P$ and $C_V$	81
8.3.3	Expansion coefficients at low temperatures	82
8.3.4		82
8.3.5	Heats of reaction from cell voltages	83
	Problems	84
9	Statistical calculation of thermodynamic quantities	86
9.1		86
	Roltzmann distribution	

_	Contents	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 Problems	98 100
10	Waves in a box	102
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
11	Systems with variable contents	113
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
12	Indistinguishable particles	120
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
13	Classical statistical mechanics	139
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
14	The problem of the equation of state	153
14.1	Intermolecular forces	153
14.2	The virial theorem	155
14.3	The second virial coefficient	158

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
15	Electric and magnetic systems	181
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
16	Fluctuations and the approach to equilibrium	199
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	202
	paramagnetic salt	
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	218
10.7	numbers	
	Problems	221
17	Transport properties	223
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
18	Phase transitions	246
18.1	Phenomena	246
18.2	The Weiss model of ferromagnetism in zero applied field	251

	Contents	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
8.10	Theories of critical point behaviour	280
	Problems	285
19	The fundamental assumptions reviewed	288
19.1	Accessibility and the ergodic assumption	288
19.2	The problem of time reversal symmetry	292
19.3	Coarse graining and the classical H-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
	Answers to problems	309
	Suggestions for further reading	313
	References	316
	Index and table of symbols	319

336

Table of constants