

Contents

1 Maxwell – Boltzmann Statistics

1.1	Thermodynamics and probability. The Boltzmann – Planck theorem	1
1.1.1	The Boltzmann – Planck theorem	5
1.2	The Maxwell – Boltzmann distribution law	7
1.2.1	Continuous Maxwell – Boltzmann distribution	14
1.3	Calculation of most probable and mean values	17
1.4	Indistinguishable molecules. The Gibbs' paradox	21
1.5	Phase volume and the number of quantum states	24
1.6	Quantum statistics	26
1.6.1	Bose – Einstein statistics	27
1.6.2	Fermi – Dirac statistics	29
1.6.3	Comparison of the three types of statistics	29
1.6.4	Degenerate ideal gas.	31
1.6.5	Applications of Bose – Einstein statistics: black-body radiation	34
1.6.6	Applications of Bose – Einstein statistics: heat capacity of solids	35

2 Ensembles, Partition Functions, and Thermodynamic Functions

2.1	Gibbs' approach, or how to avoid molecular interactions	43
2.2	The process of equilibration and increasing entropy	49
2.3	Microcanonical distribution	51
2.4	Canonical distribution	52
2.5	The probability of a macrostate	54
2.6	Thermodynamic functions derived from a canonical distribution	55
2.7	Some molecular partition functions	57
2.7.1	Degeneracy	58
2.7.2	Translational motion	59
2.7.3	Free rotation	61
2.7.4	Vibrational motion: linear harmonic oscillator	62
2.7.5	Total partition function of an ideal system	63
2.8	Fluctuations	64
2.9	Conclusions	69

3 The Law of Mass Action for Ideal Systems

3.1	The law of mass action, its origin and formal thermodynamic derivation	71
3.2	Statistical formulae for free energy	77
3.3	Statistical formulae for ideal systems	79
3.4	The law of mass action for ideal gases	81
3.4.1	Conversion to molar concentrations	83
3.4.2	Conversion to mole fractions	84
3.4.3	Standard states and standard free energies of reaction	85
3.5	The law of mass action for an ideal crystal. Spin crossover equilibria	89
3.6	Liquids	95
3.6.1	The law of mass action for an ‘ideal liquid’	97
3.7	‘Breakdown’ of the law of mass action	99
3.8	Conclusions	105

4 Reactions in Imperfect Condensed Systems. Free Volume

4.1	Additive volume: a semi-empirical model of repulsive interactions	107
4.1.1	Binary equilibrium in a liquid with repulsive interactions	108
4.1.1	Non-isomolar equilibrium in a liquid with repulsive interactions	111
4.2	Lattice theories of the liquid state	117
4.3	The Lennard-Jones and Devonshire model	119
4.4	Chemical equilibria in Lennard-Jones and Devonshire liquids	122
4.5	The non-ideal law of mass action, activities, and standard states	129
4.6	Kinetic law of mass action	135
4.7	Conclusions	143

5 Molecular Interactions

5.1	Introduction	145
5.2	Empirical binary potentials	147
5.3	Taking into account nearest, next nearest, and longer range interactions in the condensed phase	151
5.4	Frequency of vibrations	155
5.5	The shape of the potential well in a cell	157
5.6	Free volume of a Lennard-Jones and Devonshire liquid	160
5.7	Experimental determination of parameters of the Lennard-Jones potential	164
5.7.1	Compressibility: the Born – Landé method	165
5.7.2	Acoustical measurements: the B.B. Kudryavtsev method	166
5.7.3	Viscosity of gases: the Rayleigh – Chapman method	170
5.8	Conclusions	171

6 Imperfect Gases.

6.1	Introduction. The Virial Theorem	173
6.2	The Rayleigh equation	176
6.2.1	Virial coefficients: the Lennard-Jones method for the determination of the parameters of a binary potential	177
6.2.2	Free energy derived from the Rayleigh equation of state	179
6.3	A gas with weak binary interactions: a statistical thermodynamics approach	180
6.4	Van der Waals equation of state	185
6.5	Chemical equilibria in imperfect gases	188
6.5.1	Isomolar equilibria in imperfect gases	189
6.5.2	A non-isomolar reaction in an imperfect gas	192
6.5.3	Separate conditions of ideal behaviour for attractive and repulsive molecular interactions	195
6.5.4	Associative equilibria in the gaseous phase	196
6.5.5	Molecular interaction <i>via</i> a chemical reaction	198
6.6	Conclusions	200

7 Reactions in Imperfect Condensed Systems. Lattice Energy

7.1	Exchange energy	203
7.2	Non-ideality as a result of dependence of the partition function on the nature of the surroundings	205
7.3	Exchange free energy	208
7.4	Phase separations in binary mixtures	213
7.5	The law of mass action for an imperfect mixture in the condensed state	216
7.6	The regular solution model of steep spin crossover	219
7.7	Heat capacity changes in spin crossover	223
7.8	Negative exchange energy. Ordering. The Bragg – Williams approximation	226
7.9.	Description of ordering taking into account triple interactions	232
7.10	Chemical equilibrium in ordered systems. Two-step spin crossover	234
7.11	Diluted systems	240
7.12	Conclusions	246

8 Chemical Correlations

8.1	Studies of variations of chemical reactivity	249
8.1.1	Molecular parameters governing variations of chemical reactivity	250
8.1.2.	Solvent effects	252
8.1.3.	Kinetic studies	254
8.1.4	Multidimensionality of variations. Reference reactions	257
8.2	Linear free energy relationship. Modification of reactants	261
8.3	Linear free energy relationship. Variation of solvent	267
8.4	Isoequilibrium and isokinetic relationships	270
8.4.1	Statistical-mechanical model of the IER in ideal systems	273
8.4.2	The IER in gas-phase reactions	276

8.4.3 Isokinetic relationships	278
8.4.4 Non-ideality as a source of an IER	282
8.4.5 IER and exchange energy	288
8.5 Conclusions	293
9 Concluding Remarks	295
10 Appendices	
10.1 Lagrange equations and Hamilton (canonical) equations	303
10.2 Phase space	309
10.2.1 The phase space of a harmonic oscillator	310
10.2.2 The phase space of an ideal gas	311
10.3 Derivation of the canonical distribution	313
10.4 Free volume associated with vibrations	314
10.5 Rotational contribution to the equilibrium constant of the ionisation of water	316
10.6 Forms of the law of mass action employing the Γ function approximation of the factorial	317
10.7 Derivation of the van der Waals equation of state	318
10.8 Exchange energy	319
10.9 Activity coefficients derived from the non-ideality resulting from triple interactions	319
10.10 The law of mass action for a binary equilibrium in a system with non-additive volume and lattice energy	320
10.11 Physico-chemical constants and units of energy	322
11 Index	323