

CONTENTS

LIST OF SYMBOLS	IX
INTRODUCTION	XIII
CHAPTER I. CLASSICAL THERMODYNAMICS OF MIXTURES	1
1. Introduction	1
2. Thermodynamic Potentials and Fundamental Equations	2
3. Chemical Potentials	5
4. Changes of Thermodynamic Functions on Mixing	6
5. Perfect Solutions	8
6. Activity Coefficients	11
7. Excess Functions	13
8. Conditions for Phase Separation	19
CHAPTER II. STATISTICAL THERMODYNAMICS: THEOREM OF CORRESPONDING STATES AND INTERMOLECULAR FORCES	22
1. Introduction	22
2. Basic Equations of Statistical Thermodynamics – Partition function	23
3. Grand Partition Function	26
4. Theorem of Corresponding States	27
5. The Theorem of Corresponding States in Quantum Mechanics	32
6. Intermolecular Forces between Non-polar, Spherical Molecules	34
7. Intermolecular Forces in Mixtures of Spherical, Non-polar Molecules – Formal Description	42
8. Intermolecular Forces in Mixtures of Spherical, Non-polar Molecules, Validity of the Combining Rules	46
CHAPTER III. A SIMPLIFIED LATTICE MODEL	53
1. Introduction	53
2. Strictly Regular Solutions	55
3. Quasi-Chemical Approximation	59
4. General Remarks concerning the Order-Disorder Problem	64
5. Molecules of Different Sizes – Introduction	66
6. The Combinatorial Factor for Mixtures of chain molecules	69
7. Heat of Mixing	75
CHAPTER IV. CONFORMAL SOLUTIONS	78
1. Introduction	78
2. Single Component	78
3. Mixtures – Conformal Solutions	80
4. Discussion of the Theory of Conformal Solutions	85
CHAPTER V. DISTRIBUTION FUNCTIONS AND THERMODYNAMIC FUNCTIONS OF MULTICOMPONENT SYSTEMS	88
1. Introduction	88
2. Distribution Functions in the Canonical Ensemble	88
3. Distribution Functions in the Grand Canonical Ensemble	90
4. Multicomponent Systems	93

CHAPTER VI. THE ONE-DIMENSIONAL MODEL OF SOLUTIONS	99
1. Introduction	99
2. General Relations	99
3. Single Component	105
4. Equation of State of Mixtures – Excess Volume	108
5. Free Energy, Entropy and Energy	110
CHAPTER VII. THE CELL MODEL OF THE LIQUID STATE	115
1. Cell Model	115
2. Experimental Verification of the Cell Model	123
3. Smoothed Potential Cell Model	127
4. Harmonic Oscillator Cell Model	130
5. Kirkwood's Justification of the Cell Model	131
6. Multiple Occupations of Cells	136
7. Hole Theories of the Liquid State	140
8. Cell Cluster Theory	141
CHAPTER VIII. APPLICATION OF THE CELL MODEL TO SOLUTIONS OF SPHERICAL MOLECULES OF SIMILAR SIZE	147
1. Introduction	147
2. General Relations	148
3. Lennard-Jones and Devonshire Model	149
4. Smoothed Potential Cell Model	151
5. Intermolecular Forces and Excess Functions	153
CHAPTER IX. THE AVERAGE POTENTIAL MODEL FOR MIXTURES – CRUDE APPROXIMATION	156
1. Description of the Model	156
2. Average Potential	157
3. Thermodynamic Functions	160
4. A Graphical Method for the Determination of the Excess Functions	162
5. Explicit Expression for the Excess Functions in Terms of θ , δ and ρ	173
6. Influence of Pressure on the Excess Free Energy	177
7. Conclusions	179
CHAPTER X. THE AVERAGE POTENTIAL MODEL FOR MIXTURES (REFINED VERSION) LATTICE DEFORMATIONS	180
1. Description of the Refined Vernon	180
2. Average Interactions	183
3. General Formulae for the Excess Functions	185
4. Explicit Expressions for the Excess Functions	186
5. Discussion of the Excess Functions. Comparison with the Crude Approximation	190
6. Lattice Deformations	191
7. Excess Functions	195
8. Discussion of the Excess Functions. Effect of Lattice Deformations	197
9. Limitations of the Average Potential Model	200
CHAPTER XI. MIXTURES OF MOLECULES WITH SPHERICAL FIELDS OF FORCES EXPERIMENTAL EVIDENCE	204
1. Introduction	204
2. Determination of the Parameters ρ and δ	205

3. Qualitative Comparison of the Average Potential Model with the Experimental Data on Excess Functions	209
4. Discussion of Selected Systems	215
5. Discussion	229
 CHAPTER XII. CRITICAL PHENOMENA IN BINARY SYSTEMS.	233
1. Introduction	233
2. Critical Point for Pure Substances	234
3. Critical Point for Binary Mixtures	236
4. Conformal Solutions	239
5. Second Order Terms and Critical Phenomena in the Vaporization of Binary Mixtures	242
6. Explicit Form of the Second Order Terms – Discussion	247
7. Experimental Evidence	253
8. Critical Solution Phenomena	254
 CHAPTER XIII. INTERACTIONS BETWEEN POLYATOMIC MOLECULES – STRUCTURAL EFFECTS IN MIXTURES OF GLOBULAR MOLECULES	256
1. Introduction	256
2. Rough Treatments	258
3. Theorem of Corresponding States for Polyatomic Molecules	260
4. Expansion of Any Inverse Power of the Distance in a Series of Legendre Polynomials and Gegenbauer Polynomials	263
5. Interaction between Symmetric Polyatomic Molecules	269
6. Properties of Pure Globular Substances	275
7. Mixtures of Globular Molecules	279
8. Conclusions	283
 CHAPTER XIV. DIPOLAR EFFECTS IN SOLUTION – SMALL ORIENTATIONAL EFFECTS	287
1. Introduction	287
2. Pure Dipolar Substances	291
3. General Perturbation Calculation for Solutions	295
4. Applications	299
5. Comparison with Experimental Data	303
 CHAPTER XV. STRONG ORIENTATIONAL EFFECTS HYDROGEN BOND	305
1. Introduction	305
2. Theoretical Methods	309
3. Thermodynamic Properties of Associated Solutions	312
4. Spectroscopic and Thermodynamic Properties of Associated Solutions	313
5. Excess Free Energy	319
 CHAPTER XVI. STATISTICAL THERMODYNAMICS OF PURE <i>r</i> -MERS	323
1. Introduction	323
2. General Assumptions	324
3. Cell Partition Function	325
4. Cell Model for <i>r</i> -mers	331
5. Harmonic Oscillator Model	332
6. Smoothed Potential Model	334
7. Theorem of Corresponding States for <i>r</i> -mers	335
8. Application of the Theorem of Corresponding States for Hydrocarbons	337

CHAPTER XVII. POLYMER MIXTURES	348
1. Introduction	348
2. Theorem of Corresponding States for Polymer Mixtures	349
3. Average Interactions	352
4. Thermodynamic Excess Function of <i>r</i> -mer mixtures	353
5. Structural Effects in Polymer Mixtures	355
6. Explicit Expression for the Excess Free Energy	360
7. Explicit Expression for the Excess Volume	363
8. Inversion of the Excess Functions	365
9. Monomer and Dimer Mixtures	368
10. High Polymer Solutions	370
CHAPTER XVIII. QUANTUM EFFECTS IN THE LIQUID PHASE	374
1. Introduction	374
2. High temperature expansions	380
3. Ground State	382
4. Cell Model	385
5. Effect of Quantum Statistics	389
6. Isotope Effect and Intermolecular Forces	391
CHAPTER XIX. ISOTOPIC MIXTURES	393
1. Introduction – Experimental Data	393
2. Perturbation of Zero Point Energy for Harmonic Oscillators	395
3. General Discussion – Origin of the Isotope effect	400
4. Excess Functions	405
5. Solutions of Hydrogen Isotopes	408
6. Solutions of Helium Isotopes	410
7. Influence of Pressure on the Excess Properties	411
8. Graphical method for the Determination of the Excess Functions	412
9. Examples	416
10. High temperature Expansion	417
CHAPTER XX. VERY RECENT DEVELOPMENTS	419
1. Introduction	419
2. New Data on Solid and Liquid Mixtures	419
3. Critical Phenomena in Binary Systems	422
4. Hydrogen Bond	425
5. Isotopic Phase Separation	428
BIBLIOGRAPHY	430
AUTHOR INDEX	439
SUBJECT INDEX	443
CHEMICAL INDEX	447