

# Contents

Preface	v
1. Introduction	
1.1 Prolegomena	1
1.2 Concentration Units	4
2. Solution Thermodynamics of Electrolyte Solutions	11
3. Basic Electrostatics	17
3.1 Coulomb's Law	17
3.2 Poisson's Law	18
3.3 Gauss' Law	18
3.4 Relations Among the Three Laws of Electrostatics	18
4. The Debye-Hückel Theory	23
4.1 Solution of the Poisson Equation and the Debye Screened Potential	24
4.2 The Debye-Hückel Thermodynamics	30
4.2.1 The capacity	31
4.2.2 Electrostatic energy	32
5. Pitzer's Formulation for Electrolytes	39
5.1 Pitzer's Correlation for Activity Coefficients	39
5.2 Example Calculation with Pitzer's Correlation	41
5.3 Pitzer's Correlation for 2-2 Electrolytes	44
6. The Statistical Mechanics of Electrolytes	49
6.1 Basic Statistical Mechanics	49
6.2 Derivation of the Debye-Hückel Theory from Statistical Mechanics	52
6.3 Electrostatic Internal Energy from Statistical Mechanics	55
6.4 The Dielectric Constants of Solvents	56
6.4.1 The molecular-based formulas	56

6.4.2	The permittivity of mixed solvents. . . . .	57
7.	Ions as Charged Hard Spheres: The Mean Spherical Approach	61
7.1	The Mean Spherical Approach. . . . .	61
8.	The McMillan-Mayer and Lewis-Randall Scales	73
8.1	The Thermodynamic Route of Scale Conversion . . . . .	77
8.1.1	The Bjerrum relation. . . . .	79
8.1.2	The Poynting relation. . . . .	80
8.1.3	Proof of equation (8.1.18). . . . .	82
8.2	The Kirkwood-Buff Solution Theory in Scale Conversion. . . . .	84
9.	Multi-Solvent Electrolyte Solutions: Setchenov's Salting-Out Principle	89
9.1	Introduction. . . . .	89
9.2	The Setchenov Principle. . . . .	90
9.3	The Furter Correlation. . . . .	90
9.4	The Taylor Expansion of the Activity Coefficients. . . . .	93
9.5	The Gibbs-Duhem Relation for Multi-Solvent Systems . . . . .	95
9.6	The Kirkwood-Buff Solution Theory for Multi-Solvent Systems. . . . .	98
10.	Ionic Distributions: An Integral Equation Approach	103
10.1	Introduction. . . . .	103
10.2	The Ornstein-Zernike Integral Equations and their Closures . . . . .	104
10.3	The Numerical Solution Methods. . . . .	107
10.3.1	Successive substitutions – Picard's method. . . . .	108
10.3.2	Successive substitutions – in Fourier space. . . . .	112
10.3.3	Renormalization/Optimization of the direct correlation $c(r)$ . . . . .	113
10.4	The Hypernetted Chain Closure. . . . .	116
10.5	The Behavior of the Bridge Functions for Molten Salts . . . . .	123
10.6	Characterization of the Bridge Function . . . . .	127
10.6.1	Development of a theory for the bridge functions . . . . .	127
10.6.2	Renormalized bridge functions . . . . .	134
10.7	Isothermal Compressibility and Moment Rules . . . . .	139
10.7.1	Isothermal compressibility. . . . .	139
10.7.2	The zeroth moment condition: The electroneutrality. . . . .	140
10.7.3	The second moment condition. . . . .	140
11.	The Electric Double Layers	143
11.1	Introduction. . . . .	143
11.2	The Poisson-Boltzmann Equation. . . . .	145
11.3	The Gouy-Chapman Theory. . . . .	146
11.3.1	The linear Gouy-Chapman equation. . . . .	147

11.3.2	The sum rules for electrolytes at EDL . . . . .	147
11.3.2.1	The electric field at the wall . . . . .	147
11.3.2.2	The Contact value theorem. . . . .	148
11.3.2.3	Grahame's Equation. . . . .	149
11.3.3	Linear Gouy-Chapman equation—with boundary conditions .	150
11.3.4	Nonlinear Gouy-Chapman equation. . . . .	151
11.4	The Stern Layer. . . . .	153
11.5	The Zeta Potential, $\zeta$ . . . . .	156
11.6	Beyond the Poisson-Boltzmann Theory. . . . .	159
11.6.1	Ornstein-Zernike based integral equations. . . . .	159
11.6.2	The BBGKY hierarchy. . . . .	160
11.6.3	The Wertheim-Lovett-Mou-Buff equation . . . . .	160
11.6.4	The Kirkwood hierarchy. . . . .	161
11.7	The DLVO Theory. . . . .	162
11.7.1	The potential of mean force. . . . .	163
11.7.1.1	The closure relation. . . . .	163
11.7.1.2	The zero-separation theorem. . . . .	164
11.7.2	The DLVO interaction potential. . . . .	165
11.8	Beyond The DLVO Theory. . . . .	167
12.	Application: Absorption Refrigeration with Electrolytes	173
12.1	Introduction. . . . .	173
12.2	The Absorption Refrigeration Cycle. . . . .	173
12.3	The Energy Balances in the Absorption Cycle . . . . .	176
12.3.1	The individual equipment energy balance. . . . .	176
12.3.2	The coefficient of performance, COP. . . . .	177
12.4	The Thermodynamic Formulas for Enthalpy Calculation. . . . .	178
12.5	The Efficiencies and Enthalpies in Absorption Cycle. . . . .	182
12.5.1	Enthalpies and vapor pressures of electrolyte solutions. . . .	182
12.5.2	The coefficients of performance. . . . .	185
13.	Application: Amine Solutions in Acid Gas Treating	189
13.1	Introduction. . . . .	189
13.2	Overview of Acid Gas Treating. . . . .	190
13.2.1	The absorption process. . . . .	190
13.2.2	Amine solutions and chemical reactions. . . . .	193
13.3	The Thermodynamic Framework. . . . .	196
13.3.1	Hard sphere mixtures. . . . .	198
13.3.2	The Born contribution. . . . .	200
13.3.3	The activity coefficients of ions. . . . .	201
13.3.4	The activity coefficients of neutral species—UNIFAC. . . . .	201
13.4	Practical Calculations for Acid Gas Vapor Pressures. . . . .	206

13.5 Results of Amine Based Acid Gas Treating. . . . .	209
13.5.1 Acid gas loading curves. . . . .	210
13.5.2 The speciation in amine solutions. . . . .	215
13.5.3 The heat of solution of acid gases. . . . .	216
13.5.4 Hydrocarbon solubility in amine solutions. . . . .	218
13.6 Remarks on Other Acid Gas Treating Chemicals. . . . .	219
Appendices	223
Appendix I Pitzer's Parameters for Electrolyte Solutions. . . . .	224
Appendix II The Pauling Crystalline Radii. . . . .	231
Appendix III The Dielectric Constants of Selected Liquids Solvents. . . . .	232
Appendix IV Experimental Mean Activity Coefficients of NaCl & KOH Solutions. . . . .	234
Appendix V Experimental Data of Acid Gas in Amine Solutions . . . . .	236
Bibliography	243
<i>Index</i>	249
Attached Compact Disk	
<i>ElecGC</i> : Executable PC Program for Acid Gas Treating	
<i>MSA</i> : Executable PC Program for MSA Activity Coefficients	