

Contents

Theory, Techniques and Results

Chapter 1 Thermodynamics of Nonelectrolyte Solubility

Emmerich Wilhelm

1.1	Introduction	3
1.2	Thermodynamics	4
1.3	Subtleties of Approximation	8
1.4	Concluding Remarks	15
	References	15

Chapter 2 Thermodynamics of Electrolyte Solubility

Earle Waghorne

2.1	Introduction	19
2.2	The Solubility Product	20
2.3	Ion Pairing	21
2.4	Complexation	23
2.5	Electrolyte Activities	26
2.6	Pitzer Theory	28
2.7	Treatment of Non-Aqueous or Mixed Aqueous Solvents	29
	References	30

Chapter 3 Experimental, Calculated and Predicted Solubilities - Basis for the Synthesis and Design of Thermal Separation Processes

Jürgen Gmehling and Wilfried Cordes

3.1	Introduction	31
3.2	Thermodynamic Fundamentals	32
3.3	Available Solubility Data	34
3.4	Software Package (DDBSP)	34
3.5	Conclusion	39
	References	39

Chapter 4 Solubility of Gases in Ionic Liquids, Aqueous Solutions, and Mixed Solvents

Gerd Maurer and Álvaro Pérez-Salado Kamps

4.1	Introduction	41
4.2	Fundamentals	42
4.3	Experimental Arrangements	44
4.3.1	Apparatus for Measuring the Solubility of a Single Gas in a Solvent at Elevated Pressures	44
4.3.2	Apparatus for Measuring the Simultaneous Solubility of Ammonia and a Sour Gas in a Solvent at Elevated Pressures	45
4.3.3	Apparatus for Measuring the Solubility of a Sour Gas in Aqueous Solutions of Amines at Low Pressures	46
4.4	Experimental Results and Comparison with Predictions/Correlations	47
4.4.1	Gas Solubility in Ionic Liquids	47
4.4.2	Gas solubility in Aqueous Solutions of Strong Electrolytes	49
4.4.3	Solubility of Ammonia and Sour Gases in Water and Aqueous Solutions of Strong Electrolytes	51
4.4.4	Solubility of Sour Gases in Aqueous Solutions of Amines	53
4.4.5	Gas Solubility in Mixed Solvents (Water + Organic Compound)	54
4.4.6	Gas Solubility in Mixed Solvents (Water + Organic Compound + Strong Electrolyte)	55
	References	56

Chapter 5 Solubility Phenomena in “Green” Quaternary Mixtures (Ionic liquid + water + alcohol + CO₂)

Manuel Nunes da Ponte and Luís P.N. Rebelo

5.1	Introduction	59
5.2	Liquid–Liquid Equilibria: Co-Solvent Effects in Ternary Mixtures	60
5.3	Liquid–Liquid–Vapour Equilibria: The CO ₂ Anti-Solvent Effect	60
5.4	Quaternary Systems IL + Water + Alcohol + CO ₂	61
5.5	A Cascade of Phase Changes as Switching Devices for Integrated Reaction + Separation	62
	Acknowledgements	64
	References	64

Chapter 6 The Solubility of Gases in Water and Seawater*Rubin Battino and H. Lawrence Clever*

6.1	Introduction	66
6.2	Quantities Used as a Measure of Gas Solubility	67
6.3	Oxygen Solubility in Water	69
6.4	Two Related Experiments that Complement Gas Solubility Data	69
6.4.1	Partial Molar Volumes	69
6.4.2	Enthalpy Changes on Solution	70
6.5	Treatment of Data	70
6.5.1	Corrections for Non-Ideality	70
6.5.2	Temperature Dependence of Solubility – Fitting Equations	70
6.5.3	Pressure Fitting Equations	71
6.5.4	Salt Effects	71
6.6	The Solubility of Gases in Water	71
6.7	Annotated Bibliography of the Solubility of Gases in Water	74
6.8	Annotated Bibliography of the Solubility of Gases in Seawater	75
6.9	Summary	75
	References	75

Chapter 7 Isotope Effects on Solubility*W. Alexander Van Hook and Luis P.N. Rebelo*

7.1	Introduction	78
7.2	Theoretical Background	78
7.3	Liquid–Liquid Equilibria	80
7.3.1	Small Molecule Solutions Including Aqueous Systems	81
7.3.2	Polymer Systems and Polymer Solutions	86
7.4	Solubility of Gases in Liquids	88
7.5	Solubility of Ionic Solids in H ₂ O/D ₂ O	90
	Acknowledgements	91
	References	91

Chapter 8 Solubility of Organic Solids for Industry*Urszula Domańska*

8.1	Introduction	94
8.2	Solubility in Binary Systems	96
8.2.1	Solid–Liquid Equilibria in Binary Systems	98
8.2.2	Liquid–Liquid Equilibria in Binary Systems	104

8.3	Solubility in Ternary Systems	106
8.3.1	Solubility of Solids in Binary Solvent Mixtures	107
8.3.2	Solubility of Mixtures of Two Solids in a Solvent	111
8.3.3	Liquid–Liquid Equilibria in Ternary Systems	112
8.4	Correlation Methods	113
8.5	Prediction Methods	115
8.6	High-Pressure Solid–Liquid Equilibria	117
8.7	Polymers Solubility	119
8.8	Ionic Liquids Solubility	120
	References	122

Chapter 9 CO₂ Solubility in Alkylimidazolium-Based Ionic Liquids

Alireza Shariati, Sona Raeissi and Cor J. Peters

9.1	Introduction	131
9.2	Phase Behaviour	132
9.3	Molecular Interactions	141
9.4	Effect of Anion	143
9.5	Effect of Cation Alkyl Chain Length	144
9.6	Substitution at the C2 Position	144
9.7	Effects of Impurities	145
9.8	Conclusions and Summary	147
	References	148

Modelling and Simulation

Chapter 10 Solubility and Molecular Modelling

Margarida F. Costa Gomes and Agílio A.H. Pádua

10.1	Introduction	153
10.2	Thermodynamics of Solution	154
10.3	Modelling Solubility	158
10.3.1	Molecular Force Fields	160
10.3.2	Free Energy Routes	161
10.4	Solute–Solvent Interactions in Ionic Liquids	166
10.5	Conclusion	168
	Acknowledgments	168
	References	168

Chapter 11 Molecular Simulation Approaches to Solubility

Kelly E. Anderson and J. Ilja Siepmann

11.1	Introduction	171
11.2	Solubility	171

11.3	Computing Solubility for the Infinite Dilution Limit	173
11.3.1	Thermodynamic Integration	174
11.3.2	Free Energy Perturbation	175
11.3.3	Expanded Ensembles	178
11.3.4	Transition Matrix Monte Carlo	179
11.3.5	Gibbs Ensemble	179
11.3.6	Continuum Solvation Models	180
11.4	Computing the Solubility Limit	182
11.5	Finite Size Effects	183
	Acknowledgments	184
	References	184
Chapter 12	Prediction of Solubility with COSMO-RS	
	<i>Frank Eckert</i>	
12.1	Introduction	188
12.2	COSMO-RS	190
12.3	Computational Details	191
12.4	Solubility	192
12.5	Salt Solubility	195
12.6	Summary and Conclusions	198
	References	198
Industrial Applications		
Chapter 13	Solubility of Impurities in Cryogenic Liquids	
	<i>Vania De Stefani and Dominique Richon</i>	
13.1	Introduction	203
13.2	Loss of Prevention in Cryogenic Plants	204
13.3	Experimental Methods	205
13.3.1	Synthetic-Optical Method	206
13.3.2	Evaporation Method	208
13.3.3	The Static-Analytical Methods: Spectroscopic Analysis	209
13.3.4	The Static-Analytical Methods: Chromatographic Analysis	211
13.4	Review of Literature Data	212
13.5	Conclusion	217
	References	217
Chapter 14	Solubility of BTEX and Acid Gases in Alkanolamine Solutions in Relation to the Environment	
	<i>Christophe Coquelet and Dominique Richon</i>	
14.1	Introduction	219
14.2	Choice of Amine	220

14.3	Experimental Techniques	221
14.3.1	Dynamics Methods (or Flow Methods)	221
14.3.2	Static Methods	222
14.4	Experimental Results	223
14.5	Thermodynamic Frameworks	229
14.6	Conclusion	233
	Further Reading	233
	References	234
Chapter 15	Solubility of Solids in Bayer Liquors	
	<i>Erich H. Königsberger, Glenn Hefter and Peter M. May</i>	
15.1	Introduction	236
15.2	Pitzer Equations	238
15.3	Comprehensive Pitzer Model for Synthetic Bayer Liquors	240
15.4	Model Validation and Solubilities in Multi-Component Systems	241
15.5	Conclusion	246
	Acknowledgements	246
	References	246
Chapter 16	Solubility of Gases in Polymers	
	<i>Jean-Pierre E. Grolier and Severine A.E. Boyer</i>	
16.1	Introduction	249
16.2	Experimental Measurements of Gas Solubility	250
16.2.1	Gravimetric Techniques	250
16.2.2	Vibrating or Oscillating Techniques	251
16.2.3	PVT-Techniques and the Pressure Decay Method	251
16.2.4	Gas-Flow Techniques	251
16.2.5	The Coupled VW-PVT Technique	251
16.3	Experimental Evaluation of Gas Polymer Interactions and Thermophysical Properties	256
16.4	Importance of Solubility and of Associated Properties for Industrial Applications	257
16.5	Conclusion	259
	References	259
Chapter 17	Solubility in the Hydrometallurgical Leaching Process	
	<i>Toni Kaskiala, Petri Kobylin and Justin Salminen</i>	
17.1	Mineral Processing by Aqueous Solutions	261
17.2	Dissolution of Sulfidic Zinc Concentrate and Gas-Liquid Mass Transfer	262

17.3	Oxygen Solubility	267
17.4	Solubilities of Solids in Process Solutions	268
17.5	Concluding Remarks	269
	References	269
Chapter 18	Solubility Related to Reaction and Process Design	
	<i>Ralf Dohrn, Ricarda Leiberich and Ljudmila Fele Žilnik</i>	
18.1	Introduction	273
18.2	Educt Purification and Additive Introduction	274
	18.2.1 Example 1: Polyurethane Foam Quality	275
18.3	Reaction Design	276
	18.3.1 Example 2: Polyether Reaction Design	276
	18.3.2 Example 3: Chloroformate Reaction Design	278
	18.3.3 Example 4: Formaldehyde Production	280
	18.3.4 Example 5: Polyester Reaction Design	282
18.4	Separation Processes	282
	18.4.1 Example 6: Furfural Production	285
18.5	Surprising Effects of Solubilities	286
	18.5.1 Example 7: Traces of Volatile Components	288
	18.5.2 Example 8: Flame Ionization Detector (FID) Alarm at Fermentation Reactor	288
18.6	Conclusion	289
	References	290
Chapter 19	Measurements and Modelling Solid Solubilities in Supercritical Phases: Application to a Pharmaceutical Molecule, Eflucimibe	
	<i>M. Saucéau and J. Fages</i>	
19.1	Introduction	292
19.2	Experimental: Equipment and Procedures	294
19.3	Solubility in Pure CO ₂	296
19.4	Ethanol and DMSO Co-Solvent Effects	297
19.5	Modelling	300
19.6	Extension of the Chrastil Model	301
19.7	Generalizing the Mendez-Santiago and Teja Model	301
19.8	Conclusion	302
	Acknowledgements	303
	References	303
Chapter 20	Solubility in Food, Pharmaceutical, and Cosmetic Industries	
	<i>Simão Pedro Pinho and Eugénia Almeida Macedo</i>	
20.1	Introduction	305
20.2	Industrial Importance	306
20.3	Water Solubility	306

20.4	Organic and Mixed Solvent Solubility	311
20.5	Liquid–Liquid Solubility	315
20.6	Solubility in Supercritical Fluids	317
20.7	Conclusions	318
	References	319
Chapter 21	Solubility of Solids in Radioactive Waste Repositories	
	<i>Wolfgang Hummel</i>	
21.1	Introduction	323
21.2	The Safety Concept of a Geological Repository	326
21.3	Solubility of Solids in Repository Safety Assessments	329
21.4	What is the Composition of the Solution?	329
21.5	Which are the Relevant Thermodynamic Data?	331
21.6	Which are the Relevant Solid Phases?	331
	Acknowledgements	334
	References	334
Chapter 22	Carbon Dioxide in Chemical Processes	
	<i>Justin Salminen and John Prausnitz</i>	
22.1	Applications of CO ₂	337
22.2	CO ₂ In Multiphase Aqueous Systems	338
22.3	Applications in the Process Industries	341
22.4	Dynamic Systems	344
22.5	Concluding Remarks	345
	References	345
Chapter 23	Solubility and the Oil Industry	
	<i>Anthony R.H. Goodwin, Kenneth N. Marsh and Cor J. Peters</i>	
23.1	Introduction	350
23.2	Solubility Theories used in the Oil Industry	353
23.3	Experimental Methods	357
23.4	Relevance of Solubility Measurements	359
	23.4.1 Gases in Liquids	359
	23.4.2 Liquids in Gases	364
	23.4.3 Liquids in Liquids	364
	23.4.4 Gases in Solids	366
	23.4.5 Solids in Gases	367
	23.4.6 Solids in Liquids	367
	23.4.7 Gases, Liquids, and Solids	369
23.5	New Results: Solubility of Hydrogen in Normal Alkanes	370
	Acknowledgment	378
	References	378

Chapter 24 Solubility of Inorganic Salts and their Industrial Importance*Wolfgang Voigt*

24.1	Introduction	390
24.2	Oceanic Salts	391
	24.2.1 Production of K_2SO_4	394
	24.2.2 Solution Mining of Carnallite	397
24.3	Salts from Non-Oceanic Salt Lakes	398
24.4	Salt Phase Formation in Building Materials	401
24.5	Salt Hydrates for Heat Storage	402
	References	404
	Subject Index	407

