

# TOPICS IN PHYSICAL CHEMISTRY

Edited by H. Baumgärtel, E. U. Franck, W. Grünbein

On behalf of Deutsche Bunsen-Gesellschaft  
für Physikalische Chemie

## Gas Extraction

An Introduction to Fundamentals  
of Supercritical Fluids and the  
Application to Separation Processes

**G. Brunner**



**Steinkopff Darmstadt  
Springer New York**



# Contents

|                                                                                                                           |    |
|---------------------------------------------------------------------------------------------------------------------------|----|
| <b>Preface</b> .....                                                                                                      | V  |
| <br>                                                                                                                      |    |
| <b>1 Introduction</b> .....                                                                                               | 1  |
| <br>                                                                                                                      |    |
| <b>2 Properties of Supercritical and Near-Critical Gases and of Mixtures with Sub- and Supercritical Components</b> ..... | 3  |
| 2.1 What is a Supercritical Gas? .....                                                                                    | 3  |
| 2.2 Density (PVT Behavior) .....                                                                                          | 6  |
| 2.2.1 Pure Components .....                                                                                               | 6  |
| 2.2.2 Principle of Corresponding States .....                                                                             | 7  |
| 2.2.3 Analytical Equations of State .....                                                                                 | 10 |
| 2.2.4 Correlations for Pure-Component Parameters .....                                                                    | 19 |
| 2.3 Thermodynamic Properties .....                                                                                        | 21 |
| 2.4 Transport Properties .....                                                                                            | 31 |
| 2.4.1 Viscosity .....                                                                                                     | 31 |
| 2.4.1.1 Influence of Pressure on the Viscosity of Gases .....                                                             | 31 |
| 2.4.1.2 Nonpolar Gases .....                                                                                              | 34 |
| 2.4.1.3 Polar Gases .....                                                                                                 | 34 |
| 2.4.1.4 Mixtures of Gases .....                                                                                           | 35 |
| 2.4.1.5 Liquids .....                                                                                                     | 35 |
| 2.4.1.6 Viscosity of Systems with Supercritical Fluids .....                                                              | 37 |
| 2.4.2 Thermal Conductivity .....                                                                                          | 42 |
| 2.4.2.1 Gases .....                                                                                                       | 42 |
| 2.4.2.2 Liquids .....                                                                                                     | 46 |
| 2.4.3 Diffusion Coefficient .....                                                                                         | 47 |
| 2.4.3.1 Gases .....                                                                                                       | 47 |
| 2.4.3.2 Diffusion in Dense Fluids .....                                                                                   | 48 |
| 2.5 Surface Tension .....                                                                                                 | 52 |
| References .....                                                                                                          | 55 |

|          |                                                                                                                       |           |
|----------|-----------------------------------------------------------------------------------------------------------------------|-----------|
| <b>3</b> | <b>Supercritical Gases as Solvents: Phase Equilibria</b>                                                              | <b>59</b> |
| 3.1      | The Need for Phase Equilibria                                                                                         | 59        |
| 3.2      | Solubility in Supercritical Solvents                                                                                  | 60        |
| 3.3      | Phase Equilibrium in Binary Systems                                                                                   | 74        |
| 3.3.1    | Gas-liquid Equilibria of Systems,<br>Completely Miscible in the Liquid Phase                                          | 74        |
| 3.3.2    | The Critical Curve of Mixtures                                                                                        | 80        |
| 3.3.3    | Systems with Miscibility Gaps in the Condensed Phase                                                                  | 82        |
| 3.4      | Phenomenology of Binary Gas-Liquid Systems                                                                            | 88        |
| 3.5      | Phase Equilibria of Ternary Systems                                                                                   | 91        |
| 3.5.1    | Phenomenology of Ternary Systems                                                                                      | 92        |
| 3.5.2    | The Effect of a Modifier or Entrainer on Solvent Power, Selectivity,<br>and their Pressure and Temperature Dependence | 97        |
| 3.6      | Phase Equilibria of Quaternary Systems                                                                                | 105       |
| 3.7      | Multicomponent and Complex Systems                                                                                    | 113       |
| 3.7.1    | Phase Behavior of Complex Mixtures                                                                                    | 114       |
| 3.7.2    | Lumping and Pseudo-Components                                                                                         | 115       |
| 3.8      | Experimental Determination of Phase Equilibria for Gas Extraction<br>Systems                                          | 117       |
| 3.8.1    | General Remarks on Measuring Phase Equilibrium                                                                        | 117       |
| 3.8.2    | The Static Analytical Method                                                                                          | 118       |
| 3.8.3    | The Synthetic Method                                                                                                  | 123       |
| 3.8.4    | The Dynamic Method                                                                                                    | 125       |
| 3.8.5    | What is the Best Method?                                                                                              | 126       |
| 3.8.6    | Accuracy of the Measurements                                                                                          | 127       |
| 3.9      | Correlation and Calculation of Phase Equilibria and Solubilities in<br>Binary and Multicomponent Systems              | 128       |
| 3.9.1    | Basic Equations                                                                                                       | 128       |
| 3.9.2    | Equations of State for Mixtures                                                                                       | 133       |
| 3.9.3    | Predictive Calculations                                                                                               | 136       |
| 3.9.4    | Examples for Phase Equilibrium Calculations                                                                           | 137       |
|          | <i>References</i>                                                                                                     | 144       |

|          |                                                                |            |
|----------|----------------------------------------------------------------|------------|
| <b>4</b> | <b>Heat and Mass Transfer</b>                                  | <b>147</b> |
| 4.1      | Heat Transfer                                                  | 147        |
| 4.1.1    | Conductive Heat Transfer                                       | 147        |
| 4.1.2    | Heat Transfer by Convection                                    | 148        |
| 4.1.3    | Boiling                                                        | 152        |
| 4.1.4    | Dimensionless Correlations for Heat Transfer Including Boiling | 155        |

|           |                                                                                                    |            |
|-----------|----------------------------------------------------------------------------------------------------|------------|
| 4.1.5     | Reductive Parameters for Dimensionless Correlations . . . . .                                      | 158        |
| 4.2       | Mass Transfer . . . . .                                                                            | 158        |
| 4.2.1     | Influence of Pressure and Gravity . . . . .                                                        | 158        |
| 4.2.2     | Solid-gas Systems . . . . .                                                                        | 160        |
| 4.2.3     | Liquid-gas Systems . . . . .                                                                       | 162        |
|           | <i>References</i> . . . . .                                                                        | 163        |
| <br>      |                                                                                                    |            |
| <b>5.</b> | <b>Solvent cycle</b> . . . . .                                                                     | <b>165</b> |
| 5.1       | Gas Circuit in the Compressor Mode . . . . .                                                       | 166        |
| 5.2       | Solvent Circuit in the Pumping Mode . . . . .                                                      | 170        |
| 5.3       | Comparison of Compressor and Pump Cycle . . . . .                                                  | 173        |
|           | <i>References</i> . . . . .                                                                        | 174        |
| <br>      |                                                                                                    |            |
| <b>6</b>  | <b>The Separation of Solvent and Dissolved Substances:<br/>Methods for Precipitation</b> . . . . . | <b>175</b> |
| 6.1       | Separation by Reduced Solvent Power . . . . .                                                      | 175        |
| 6.1.1     | Reducing Pressure and Increasing Temperature . . . . .                                             | 175        |
| 6.1.2     | Separation by Expansion into the Two-Phase Region of the<br>Supercritical Solvent . . . . .        | 176        |
| 6.2       | Separation of Phases: Improved Separation by Cyclones . . . . .                                    | 176        |
| 6.3       | Separation of Extract and Solvent by a Mass Separating Agent . . . . .                             | 177        |
| 6.3.1     | Separation by Absorption . . . . .                                                                 | 177        |
| 6.3.2     | Separation by Adsorption . . . . .                                                                 | 177        |
| 6.3.3     | Separation by Membranes . . . . .                                                                  | 178        |
| 6.3.4     | Separation by Adding a Substance of Low Solvent Power . . . . .                                    | 178        |
|           | <i>References</i> . . . . .                                                                        | 178        |
| <br>      |                                                                                                    |            |
| <b>7</b>  | <b>Extraction of Substances with Supercritical<br/>Fluids from Solid Substrates</b> . . . . .      | <b>179</b> |
| 7.1       | Introduction . . . . .                                                                             | 179        |
| 7.2       | The Extraction Process . . . . .                                                                   | 180        |

|         |                                                                                                               |     |
|---------|---------------------------------------------------------------------------------------------------------------|-----|
| 7.2.1   | General Description of the Extraction Process and an Extraction Plant                                         | 180 |
| 7.2.2   | Mechanisms of Transport in the Solid Phase                                                                    | 181 |
| 7.2.3   | Course of the Extraction of Substances from Solids<br>with Supercritical Solvents                             | 185 |
| 7.2.3.1 | Total Amount of Extract                                                                                       | 185 |
| 7.2.3.2 | Extraction Rate                                                                                               | 188 |
| 7.2.3.3 | Remaining Amount of Extract in the Solid                                                                      | 189 |
| 7.2.3.4 | Concentration of the Extract in the Supercritical Solvent                                                     | 190 |
| 7.2.4   | Influence of Process Parameters and the Condition of the<br>Solid Substrate on the Extracting Process         | 192 |
| 7.3     | Modeling the Extraction                                                                                       | 199 |
| 7.3.1   | Basic Considerations                                                                                          | 200 |
| 7.3.2   | Steady State Approximation of the Extraction from Solids                                                      | 200 |
| 7.3.3   | More Complex Models for the Extraction from Solids:<br>The One-Dimensional Dispersion – Single Particle Model | 202 |
| 7.3.4   | Particle Model                                                                                                | 204 |
| 7.3.5   | Coupling Condition between Fluid Phase Model and Particle Model                                               | 205 |
| 7.3.6   | Dimensionless Groups                                                                                          | 206 |
| 7.3.7   | Some Aspects for Modeling the Fluid Phase                                                                     | 206 |
| 7.3.7.1 | Hydrodynamic Behavior and Axial Dispersion                                                                    | 206 |
| 7.3.7.2 | Model without Axial Dispersion                                                                                | 210 |
| 7.3.8   | Some Aspects for Modeling the Solid Phase                                                                     | 212 |
| 7.3.8.1 | Concentration Gradients in Fixed Bed of Particles                                                             | 212 |
| 7.3.8.2 | Determination of the Effective Diffusion Coefficient                                                          | 214 |
| 7.3.8.3 | Modeling the Extraction by Means of Special Solutions of Fick's<br>Second Law                                 | 215 |
| 7.3.8.4 | Simplification of the Mass Balance for the Solid Phase                                                        | 222 |
| 7.3.9   | The VTII-Model for the Extraction from Solids Using Supercritical<br>Solvents                                 | 224 |
| 7.4     | Examples                                                                                                      | 227 |
| 7.4.1   | Extraction of Theobromine from Cocoa Seed Shells                                                              | 227 |
| 7.4.2   | Extraction of Oil from Oil Seeds                                                                              | 231 |
| 7.4.3   | Comparison of Extracts from Liquid Extraction and Extraction with<br>Supercritical Carbon Dioxide.            | 237 |
| 7.4.4   | Solids in Multiple Stages and Countercurrent Operation in Gas<br>Extraction from Solids                       | 238 |
| 7.5     | Laboratory and Pilot Plant Equipment                                                                          | 240 |
| 7.5.1   | General Considerations                                                                                        | 240 |
| 7.5.2   | Screening Unit                                                                                                | 242 |
| 7.5.3   | Laboratory Extraction Plant, Small Extraction Volume                                                          | 243 |
| 7.5.4   | Laboratory Extraction Plant, Large Extraction Volume                                                          | 245 |
| 7.5.5   | Pilot Plant                                                                                                   | 247 |
|         | <i>References</i>                                                                                             | 248 |

|          |                                                                                                            |            |
|----------|------------------------------------------------------------------------------------------------------------|------------|
| <b>8</b> | <b>Countercurrent Multistage Extraction</b>                                                                | <b>251</b> |
| 8.1      | Basic Considerations                                                                                       | 251        |
| 8.1.1    | Countercurrent Processing                                                                                  | 251        |
| 8.1.2    | The Extraction Process                                                                                     | 251        |
| 8.1.3    | Design Considerations and Basic Equations                                                                  | 253        |
| 8.1.4    | Some Additional Considerations                                                                             | 255        |
| 8.2      | Modeling Countercurrent Gas Extraction                                                                     | 258        |
| 8.2.1    | The Concept of Equilibrium or Theoretical Stages                                                           | 258        |
| 8.2.2    | General Equations                                                                                          | 259        |
| 8.2.3    | Reduction of Multicomponent and Complex Mixtures to Equivalent Binary, Ternary or Quaternary Systems       | 261        |
| 8.2.4    | Number of Theoretical Stages for a Binary or Equivalent Binary System                                      | 262        |
| 8.2.5    | Analysis of Countercurrent Gas Extraction According to the McCabe-Thiele Method                            | 264        |
| 8.2.5.1  | Determination of Operating Lines                                                                           | 265        |
| 8.2.5.2  | Determination of Theoretical Stages                                                                        | 267        |
| 8.2.5.3  | Limiting Operating Conditions for the Amount of Countercurrent Flows                                       | 268        |
| 8.2.5.4  | Consideration of Equilibrium Data                                                                          | 268        |
| 8.2.6    | Analysis with the KSB-Equations                                                                            | 271        |
| 8.2.7    | Including the Supercritical Solvent into the Analysis of the Separation Process                            | 272        |
| 8.2.8    | Ponchon-Savarit Method for an Equivalent Ternary System                                                    | 273        |
| 8.2.9    | The NTU-HTU Method                                                                                         | 276        |
| 8.2.10   | Analysis of Countercurrent Gas Extraction                                                                  | 277        |
| 8.3      | The Separation of Fatty Acids According to Chain Length and Saturation                                     | 278        |
| 8.3.1    | Background                                                                                                 | 278        |
| 8.3.2    | Feed                                                                                                       | 279        |
| 8.3.3    | Analytical Conditions                                                                                      | 280        |
| 8.3.4    | Phase Equilibria                                                                                           | 280        |
| 8.3.5    | Selection of Process Conditions                                                                            | 284        |
| 8.3.6    | Results of Separation Experiments                                                                          | 285        |
| 8.3.7    | Analysis of the Separation                                                                                 | 287        |
| 8.4      | Tocopherols                                                                                                | 290        |
| 8.4.1    | Background                                                                                                 | 290        |
| 8.4.2    | Feed Mixture (Initial System of Components)                                                                | 291        |
| 8.4.3    | Analytical Conditions                                                                                      | 293        |
| 8.4.4    | Phase Equilibria                                                                                           | 293        |
| 8.4.5    | Reduction of Number of Components, Selection of Key Components, Separation Sequence and Process Conditions | 296        |
| 8.4.6    | Results of Separation Experiments                                                                          | 297        |

|       |                                                                                       |     |
|-------|---------------------------------------------------------------------------------------|-----|
| 8.5   | Countercurrent Gas Extraction with a Co-Solvent . . . . .                             | 300 |
| 8.5.1 | Basic Considerations . . . . .                                                        | 300 |
| 8.5.2 | Countercurrent Gas Extraction with a Co-Solvent as<br>Quasi-ternary Mixture . . . . . | 302 |
| 8.6   | Laboratory Plants and Equipment . . . . .                                             | 305 |
| 8.6.1 | Laboratory Plant 1 . . . . .                                                          | 306 |
| 8.6.2 | Laboratory Plant 2 . . . . .                                                          | 308 |
|       | <i>References</i> . . . . .                                                           | 310 |

## 9      **Chromatography with Supercritical Fluids (Supercritical Fluid Chromatography, SFC)** . . . . . 313

|       |                                                                                            |     |
|-------|--------------------------------------------------------------------------------------------|-----|
| 9.1   | Chromatographic Fundamentals . . . . .                                                     | 313 |
| 9.1.1 | Chromatography as Separation Process . . . . .                                             | 313 |
| 9.1.2 | Mode of Operation of Chromatographic Separations . . . . .                                 | 314 |
| 9.1.3 | The Mobile Phase . . . . .                                                                 | 320 |
| 9.1.4 | Scale of Chromatographic Separations . . . . .                                             | 327 |
| 9.1.5 | Methods for Scaling up Chromatography . . . . .                                            | 328 |
| 9.2   | Practical Verification of SFC . . . . .                                                    | 331 |
| 9.2.1 | Description of an SFC: General Design . . . . .                                            | 331 |
| 9.2.2 | Injection Techniques . . . . .                                                             | 332 |
| 9.2.3 | Columns . . . . .                                                                          | 334 |
| 9.2.4 | Detectors . . . . .                                                                        | 337 |
| 9.2.5 | Expansion of the Mobile Phase and Sample Collecting System . . . . .                       | 338 |
| 9.3   | Theoretical Description of SFC with Special Consideration of Scale-up . . . . .            | 340 |
| 9.3.1 | Fundamental Thermodynamic Equations . . . . .                                              | 340 |
| 9.3.2 | Number of Theoretical Stages in Chromatographic Separations . . . . .                      | 343 |
| 9.3.3 | Theories for Scale-up . . . . .                                                            | 351 |
| 9.4   | Supercritical Fluid Chromatography (SFC) on a Preparative Scale:<br>Two Examples . . . . . | 358 |
| 9.4.1 | General Approach . . . . .                                                                 | 358 |
| 9.4.2 | Separation of Prostaglandins . . . . .                                                     | 360 |
| 9.4.3 | Separation of Tocopherols . . . . .                                                        | 368 |
| 9.5   | On-line Analysis with SFC . . . . .                                                        | 377 |
|       | <i>References</i> . . . . .                                                                | 380 |

## 10      **Conclusion** . . . . . 383

## **Subject Index** . . . . . 385