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Introduction

Process simulation is a tool for the development, design, and optimization of processes in the chemical, petrochemical, pharmaceutical, energy-producing, gas processing, environmental, cosmetics and food industry. It provides a representation of the particular basic operations of the process using mathematical models for the different unit operations, ensuring that the mass and energy balances are maintained. Nowadays, simulation models are of extraordinary importance for scientific and technical developments and even for economic and political decisions, as it is, for example, the case in the climate modeling. Unfortunately, the wide and productive use of process simulation in industry is currently being limited by a lack of understanding of thermodynamics and its application in process simulation. This book is dedicated to provide this knowledge in a convenient way.

The development of process simulation started in the 1960s, when appropriate hardware and software became available and could connect the remarkable knowledge about thermophysical properties, phase equilibria, reaction equilibria, reaction kinetics, and particular unit operations. A number of comprehensive simulation programs have been developed, commercial ones (Aspen Plus, ChemCAD, HYSYS, PRO/II, ProSim, and SYSTEM 7) as well as in-house simulators in large companies, for example, VTPlan (Bayer AG) or CHEMASIM (BASF), not to mention the large number of in-house tools that cover the particular calculation tasks of small companies working in process engineering. Nevertheless, what all the simulators have in common is that they are only as good as the models and the corresponding model parameters available. Most of the process simulators provide a default data bank for the user, but finally the user himself/herself is responsible for the parameters used. In this context, it is very useful that since the 1970s data banks for pure component and mixture data (e.g. DIPPR, DDB) have been compiled. Today even the data formats are well established so that they can easily be interpreted by computer programs. These activities belong to the main fundamentals of modern process simulation. Furthermore, these systematic data collections made it possible to develop prediction methods like ASOG, UNIFAC, modified UNIFAC, PSRK, and VTPR, which made it possible for the process engineers to adjust reasonable parameters even for systems where no data are available. One of the most important purposes of this book is to enable the user to choose the model and the model parameters in an appropriate way.

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Various degrees of effort can be applied in process simulation. A simple split balance can give a first overview of the process without introducing any physical relationships into the calculation. The user just defines split factors to decide which way the particular components take. In a medium level of complexity, shortcut methods are used to characterize the various process operations. The rigorous simulation with its full complexity can be considered as the most common case. The particular unit operations (reactors, columns, heat exchangers, flash vessels, compressors, valves, pumps, etc.) are represented with their correct physical background and a model for the thermophysical properties.

Different physical modes are sometimes available for the same unit operation. A distillation column can, for example, be modeled on the basis of theoretical stages or using a rate-based model, taking into account the mass transfer on the column internals. A simulation of this kind can be used to extract the data for the design of the process equipment or to optimize the process itself. During recent years, dynamic simulation has become more and more important. In this context, *dynamic* means that the particular input data can be varied with time so that the time-dependent behavior of the plant can be modeled and the efficiency of the process control can be evaluated.

For both steady-state and dynamic simulations, the correct representation of thermophysical properties, phase equilibria, mass transfer, and chemical reactions mainly determines the quality of the simulation. As those are strongly influenced by thermodynamic relationships, a correct application of chemical thermodynamics is an indispensable requirement for a successful process simulation. This includes the handling of raw data to obtain pure component and mixture parameters with a sufficient quality as well as the choice of an appropriate model and the ability to assess the capabilities of the particular models. Poor thermophysical property data or data of insufficient availability, inappropriate models and model parameters, and a missing perception about the sensitivities are among the most common mistakes in process simulation and can lead to a wrong equipment design. Creative application of thermodynamic knowledge can result in the development of feasible and elegant process alternatives, which makes thermodynamics an essential tool for business success in the industries mentioned above.

However, one must be aware that there are a lot of pitfalls beyond thermodynamics. Unknown components, foam formation, slow mass transfer, fouling layers, decomposition, or side reactions might lead to unrealistic results. The occurrence of solids in general is always a challenge, where only small scale-ups are possible ($\sim$1 : 10) in contrast to fluid processes, where a scale-up of 1 : 1000 is nothing unusual. For crystallization, the kinetics of crystal growth is often more important than the phase equilibrium itself. Nevertheless, even under these conditions simulation can yield a valuable contribution for understanding the principles of a process.

Nowadays, process simulations are the basis for the design of plants and the evaluation of investment and operation costs, as well as for follow-up tasks like process safety analysis, emission lists, or performance evaluation. For process development and optimization purposes, they can effectively be used to compare various options and select the most promising one, which, however,

should in general be verified experimentally. Therefore, a state-of-the-art process simulation can make a considerable contribution for both plant contractors and operating companies in reducing costs.

The structure of this book is as follows:

In Chapter 2, the particular phenomena of the behavior of fluids are introduced and explained for pure fluids. The main types of equations of state and their abilities are described. In Chapter 3, the various quantities of interest in process simulation and their correlation and prediction are discussed in detail.

In Chapter 4, the important terms for the description of the thermodynamics of mixtures are explained, including the g^E mixing rules, which have become the main progress of modern equations of state for mixtures.

Chapter 5 gives a comprehensive overview on the most important models and routes for phase equilibrium calculation, including sophisticated phenomena like the pressure dependence of liquid–liquid equilibria. The abilities and weaknesses of both g^E models and equations of state are thoroughly discussed. A special focus is dedicated to the predictive methods for the calculation of phase equilibria, applying the UNIFAC group contribution method and its derivatives, that is, the modified UNIFAC method and the PSRK and VTPR group contribution equations of state. Furthermore, in Chapter 6 the calculation of caloric properties and the way they are treated in process simulation programs are explained.

While Chapter 5 deals with models which are applicable to a wide variety of nonelectrolyte systems, separate chapters have been composed where systems that require specialized models are described. These are electrolytes (Chapter 7), polymers (Chapter 10), and systems where chemical reactions and phase equilibrium calculations are closely linked, for example, aqueous formaldehyde solutions and substances showing vapor phase association (Chapter 13). Special phase equilibria like solid–liquid equilibria and osmosis are discussed in Chapters 8 and 9, respectively.

Certain techniques for the application of thermodynamics in separation technology are introduced in Chapter 11, for example, the concept of residue curve maps, a general procedure for the choice of suitable solvents for the separation of azeotropic systems, the verification of model parameters prior to process simulation, and the identification of separation problems.

Chapter 12 gives an extensive coverage on the thermodynamics of chemical reactions, which emphasizes the importance of the real mixture behavior on the description of reaction equilibria and the enthalpies of reaction as well as solvent effects on chemical equilibrium conversion.

Chapter 14 introduces some standard calculations frequently used in process simulation and design.

Chapter 15 concludes the book with the explanation of some widely used measurement techniques for the determination of unknown phase equilibria and physical properties.

The book is supplemented by a large appendix, listing parameters for the calculation of thermophysical properties and increasing the understanding by the accurate derivation of some relationships. To enable the reader to set up his or her own models, special care was taken to explain the regression procedures and

philosophies in the Appendix, both for pure component properties and for the adjustment of binary parameters.

All the topics are illustrated with examples that are closely related to practical process simulation problems. At the end of each chapter, additional calculation examples are given to enable the reader to extend his or her comprehension. An introduction to a larger number of problems can be found in Chapter 16. These problems and their solutions can be downloaded from the site www.ddbst.com. The problems partially require the use of the software Mathcad® and the Dortmund Data Bank Software Package – Explorer Version. Both packages can be downloaded from the Internet. The DDBSP Explorer Version is free to use, whereas Mathcad is only available for free during a tryout period of 30 days. Mathcad files enable the users to perform the iterative calculations themselves and get a feeling for their complexity. Often, typical pitfalls in process simulation are covered in the examples, which should be helpful for the reader to avoid them in advance.

Special care was taken to deliver a complete logical representation of chemical thermodynamics. As much as possible, derivations for the particular relationships have been provided to ensure a proper understanding and to avoid mistakes in their application. Many of these derivations have been put into the Appendix in order not to interrupt the flow of the text.