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COMPUTER CALCULATIONS FOR MULTICOMPONENT VAPOR-LIQUID AND LIQUID-LIQUID EQUILIBRIA

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Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria

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Preface

Separation of fluid mixtures constitutes one of the main tasks of chemical engineering. While new separation methods are under active development, most large-scale separations are achieved by classical phase-contacting operations: distillation, absorption, stripping and extraction. Design of equipment for such operations requires quantitative estimates of phase equilibria.

This monograph presents a detailed discussion of a molecular-thermodynamic method for computer-implemented estimation of vapor-liquid and liquid-liquid equilibria in multicomponent systems, coupled with a minimum of experimental information. Attention is confined to nonelectrolytes, i.e. organic liquids (hydrocarbons and their derivatives, alcohols, nitriles, ketones, esters, etc.) and a few common inorganic fluids such as water and carbon dioxide. Attention is also confined to low or moderate pressures and to conditions remote from critical.

Our earlier monograph, "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," published in 1967, is now out of date. The material presented here is, in a sense, an updating of the earlier work, but it is also a major extension since the present monograph, unlike the former, discusses also liquid-liquid equilibria and presents generalized iterative techniques for equilibrium calculations.

No overall statement can be made concerning the accuracy of the calculated results because that depends crucially on the accuracy of the limited experimental data on which the calculations, inevitably, must rest. When these data are accurate and when careful attention is given to all limitations specified throughout the monograph, the calculated results are likely to be reliable.

It is a pleasure to record my gratitude first, to my co-authors at the University of Illinois, Charles Eckert and Richard Hsieh,* who provided much of the material on pure-component properties and enthalpies; and to John O'Connell, University of Florida, who provided much of the material on gas-

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*Now at Chevron Research Company, Richmond, California.

phase nonideality and on liquid mixtures containing one or more supercritical components; second, to my Berkeley colleague, Edward Grens, who developed all the computational procedures and programs, and finally, to my former graduate student and coworker, Thomas Anderson,** who performed the illustrative calculations, prepared the figures and took care of all the many details that are required in the preparation of a monograph. Much of the material in Chapter 4 is taken from Tom's doctoral dissertation. Most important, it was Tom's consistent cheerfulness and his willingness to undertake numerous time-consuming tasks which sustained the momentum of our work and which enabled us to bring it to conclusion.

Special thanks also go to Harold Null (Monsanto Company, St. Louis, Missouri) and Carl Deal (Shell Development Company, Houston, Texas) for their constructive review of the manuscript, to Eldon Larsen for his generous help in attending to the details of preparing the final version, and to Diana Lorentz for her conscientious typing services.

Molecular thermodynamics is progressing rapidly; similarly, new developments in computer science are certain to continue. It is likely, therefore, that the techniques discussed in this monograph will be modified, perhaps drastically so, as new understanding of mixtures and new computing possibilities become available. The techniques presented here, however, reflect the current state-of-the-art for combining thermodynamics, molecular physics and computer science for chemical process design.

All computer subroutines and parameter compilations (single component and binary) presented in this monograph can be obtained on magnetic tapes; interested readers should write to me for details. Available are 7-track tapes at 800 bpi, in unblocked BCD with 80-character (card-image) records. It may also be possible to furnish certain types of 9-track tapes on special request. All subroutines are written in American National Standard FORTRAN (FORTRAN IV), ANSI X309-1978; these are compatible with most computer systems. The sample main programs presented in the text require minor modifications for use with many computer systems; these modifications, however,

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are not included on the tape.

It is my hope--and that of my co-authors--that this monograph may find useful application by process design engineers, that it may stimulate graduate students and research workers toward seeking new techniques which improve upon those presented here, and that all who use this monograph, for whatever purpose, may derive a sense of satisfaction, as the authors have, in combining rational thought and scientific imagination toward the solution of practical problems.

Berkeley, California

John Prausnitz

Contents

Chapter 1

INTRODUCTION

Design of chemical processes almost always includes design for separation operations; the most common of these are distillation, absorption, and extraction.

One of the essential ingredients for rational design of such separation operations is a knowledge of the required phase equilibria. The purpose of the present monograph is to present a technique, implemented for digital computers, to estimate these equilibria from a minimum of experimental information.

While much attention has been given to the development of computer techniques for design of distillation and absorption columns, much less attention has been devoted to the development of such techniques for equipment using liquid-liquid extraction. However, regardless of the nature of the operation, few systematic attempts have been made to organize phase-equilibrium information for direct use in chemical process design. This monograph presents a systematic procedure for calculating multicomponent vapor-liquid and liquid-liquid equilibria for mixtures commonly encountered in the chemical process industries. Attention is limited to systems at low or moderate pressures. Pertinent references to previous work are given at the end of this chapter.

Need for a Thermodynamic Treatment

The possible number of liquid and vapor mixtures in technological processes is incredibly large, and it is unreasonable to expect that experimental vapor-liquid and liquid-liquid equilibria will ever be available for a significant fraction of this number. Further, obtaining good experimental data requires appreciable experimental skill, experience, and patience. It is, therefore, an economic necessity to consider techniques for calculating phase equilibria for multicomponent mixtures from few experimental data. Such techniques should require only a limited experimental effort and, whenever possible, should be based on a theoretical foundation to provide reliability for interpolation and extrapolation with respect to temperature, pressure, and composition.

Vapor-liquid and liquid-liquid equilibria depend on the nature of the components present, on their concentrations in both phases, and on the temperature and pressure of the system. Because of the large number of variables which determine multicomponent equilibria, it is essential to utilize an efficient organizational tool which reduces available experimental data to a small number of theoretically significant functions and parameters; these functions and parameters may then be called upon to form the building blocks upon which to construct the desired equilibria. Such an organizational tool is provided by thermodynamic analysis and synthesis. First, limited pure-component and binary data are analyzed to yield fundamental thermodynamic quantities. Second, these quantities are reduced to obtain parameters in a molecular model. That model, by synthesis, may be used to calculate the phase behavior of multicomponent liquids and vapors. In this way, it is possible to "scale up" data on binary and pure-component systems to obtain good estimates of the properties of multicomponent mixtures of a large variety of components including water, polar organic solvents such as ketones, alcohols, nitriles, etc., and paraffinic, naphthenic, and aromatic hydrocarbons.

The method proposed in this monograph has a firm thermodynamic basis. For vapor-liquid equilibria, the method may be used at low or moderate pressures commonly encountered in separation operations since vapor-phase nonidealities are taken into account. For liquid-liquid equilibria the effect of pressure is usually not important unless the pressure is very large or unless conditions are near the vapor-liquid critical region.

The detailed techniques presented here are based on particular models for the vapor phase (Hayden-O'Connell) and for the liquid phase (UNIQUAC). However, our discussion of these techniques is sufficiently general to allow the use of other models, whenever the user prefers to do so.

Solution of Simultaneous Thermodynamic Equations

In vapor-liquid equilibria, if one phase composition is given, there are basically four types of problems, characterized by those variables which are specified and those which are to be calculated. Let T stand for temperature, P for total pressure, x_i for the mole fraction of component i in the liquid phase, and y_i for the mole fraction of component i in the vapor phase. For a mixture containing m components, the four types can be organized in this way:

Given	Find
$P, x_1 x_2 \ldots x_m$	$T, y_1 y_2 \ldots y_m$
$T, x_1 x_2 \ldots x_m$	$P, y_1 y_2 \ldots y_m$
$P, y_1 y_2 \ldots y_m$	$T, x_1 x_2 \ldots x_m$
$T, y_1 y_2 \ldots y_m$	$P, x_1 x_2 \ldots x_m$

In each of these problems, there are m unknowns; either the pressure or the temperature is unknown and there are m - 1 unknown mole fractions.

When only the total system composition, pressure, and temperature (or enthalpy) are specified, the problem becomes a flash calculation. This type of problem requires simultaneous solution of the material balance as well as the phase-equilibrium relations.

In liquid-liquid equilibria, the total composition and temperature are known; the pressure is usually not important. This problem is similar in some ways to a vapor-liquid flash and here is referred to as a liquid-liquid flash calculation.

For vapor-liquid equilibria, the equations of equilibrium which must be satisfied are of the form

$$f_i^V = f_i^L \qquad (1\text{-}1)$$

where f_i^V is the fugacity of component i in the vapor phase and f_i^L is that in the liquid phase. There are m equations of the form (1). The fugacity f_i^V is a function of $T, P, y_1 \ldots y_m$ and the fugacity f_i^L is a function of $T, P, x_1 \ldots x_m$. Once these functions are established, the problem is, in principle, solved. The solution of these m simultaneous equations, however, requires tedious iterative calculations which can be effectively carried out only by an electronic computer.

In liquid-liquid equilibria, the equations of equilibrium which must be satisfied are of the form

$$f'_i = f''_i \tag{1-2}$$

where f'_i, the fugacity of component i in the ' phase, is a function of $T,P,x'_1 \ldots x'_m$ and f''_i, the fugacity of component i in the " phase, is a function of $T,P,x'' \ldots x''_m$.[†] There are m equations of the form (2). Once these functions are established, the problem is, in principle, solved. However, for multicomponent liquid-liquid equilibria, the computational problems are much more severe than those encountered in multicomponent vapor-liquid equilibria.

In vapor-liquid equilibria, it is relatively easy to start the iteration because assumption of ideal behavior (Raoult's law) provides a reasonable zeroth approximation. By contrast, there is no obvious corresponding method to start the iteration calculation for liquid-liquid equilibria. Further, when two liquid phases are present, we must calculate for each component activity coefficients in <u>two</u> phases; since these are often strongly nonlinear functions of compositions, liquid-liquid equilibrium calculations are highly sensitive to small changes in composition. In vapor-liquid equilibria at modest pressures, this sensitivity is lower because vapor-phase fugacity coefficients are usually close to unity and only weak functions of composition. For liquid-liquid equilibria, it is therefore more difficult to construct a numerical iteration procedure that converges both rapidly and consistently.

[†] For typical conditions in the chemical industry, the effect of pressure on liquid-liquid equilibria is negligible and therefore in this monograph pressure is not considered as a variable in Equation (2).

In Chapter 2 we discuss briefly the thermodynamic functions whereby the abstract fugacities are related to the measurable, real quantities: temperature, pressure, and composition. This formulation is then given more completely in Chapters 3 and 4, which present detailed material on vapor-phase and liquid-phase fugacities, respectively.

Accuracy

The accuracy of our calculations is strongly dependent on the accuracy of the experimental data used to obtain the necessary parameters. While we cannot make any general quantitative statement about the accuracy of our calculations for multicomponent vapor-liquid equilibria, our experience leads us to believe that the calculated results for ternary or quarternary mixtures have an accuracy only slightly less than that of the binary data upon which the calculations are based. For multicomponent liquid-liquid equilibria, the accuracy of prediction is dependent not only upon the accuracy of the binary data, but also on the method used to obtain binary parameters. While there are always exceptions, in typical cases the technique used for binary-data reduction is of some, but not major, importance for vapor-liquid equilibria. However, for liquid-liquid equilibria, the method of data reduction plays a crucial role, as discussed in Chapters 4 and 6.

Computer Implementation

The calculation of vapor and liquid fugacities in multicomponent systems has been implemented by a set of computer programs in the form of FORTRAN IV subroutines. These are applicable to systems of up to twenty components, and operate on a thermodynamic data base including parameters for 92 compounds.[†] The set includes subroutines for evaluation of vapor-phase fugacity

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[†] The data base contains provisions for a simple augmentation by up to eight additional compounds or substitution of other compounds for those included. Binary interaction parameters necessary for calculation of fugacities in liquid mixtures are presently available for 180 pairs.