vapor-liquid equilibria
using UNIFAC

a group-contribution method

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H_2O $-CH_2-$ $-CH_2CN$ $-COO$

$-COOH$ $-CH_2-O-$ $-CHCl_2$

CH_2Cl $-CH_2CO-$ $-CH_2CH_2$

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PREFACE

by the authors

The UNIFAC method is based on and at the same time the result of contributions by different groups. The authors wish to express their sincere thanks to Professor J.M. Prausnitz for his constant encouragement and helpful criticism in the further development of UNIFAC, which originated from his laboratory. We thank Professor H.C. Van Ness for carefully reading the manuscript and for constructive comments; Professor J.P. O'Connell for supplying useful information on the Hayden-O'Connell correlation; M.L. Michelsen for his collaboration in developing the distillation programs; and Professor U. Onken for his support of the project.

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PREFACE

by

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The most common operation in chemical industry is the separation of liquid mixtures through distillation. Efficient design of distillation equipment requires quantitative understanding of vapor-liquid equilibria in multicomponent mixtures as expressed through vapor-phase fugacity coefficients and liquid-phase activity coefficients. At low or modest pressures, fugacity coefficients can be estimated easily but, except for very simple mixtures, experimental mixture data are required to calculate activity coefficients.

Since the variety of liquid mixtures in chemical technology is extremely large, it is not likely that necessary experimental data will always be available for every mixture of interest. It is therefore desirable to correlate limited experimental data in such a way as to enable the chemical engineer to predict with confidence the activity coefficients in those mixtures where little or no experimental data are available. For non-electrolyte mixtures, a procedure for establishing such a correlation is provided by the concept of group contributions. In this concept, each molecule is considered as the sum of the functional groups (e.g., methylene, nitro, keto, amino, carboxyl) which constitute that molecule; the thermodynamic properties of a solution are then correlated, not in terms of the molecules, but rather in terms of the functional groups which comprise the mixture. The large advantage of this concept is that whereas the number of different molecules in chemical technology is very large, these molecules can be constituted from a much smaller number of functional groups.

A particularly promising method for calculating activity coefficients from group contributions is provided by UNIFAC, as described in this monograph. This method is a consequence of a model for activity coefficients called UNIQUAC (Universal

Quasi-Chemical) which, in turn, represents a reasonable attempt to generalize to molecules of different size and shape Guggenheim's quasi-chemical theory of strongly nonideal liquid mixtures. The word UNIFAC stands for UNIQUAC Functional-group Activity Coefficients.

The UNIQUAC model was proposed by Denis Abrams in Berkeley in 1974 and shortly thereafter Aage Fredenslund came to Berkeley to work with Russell Jones on the group-contribution model which UNIQUAC had suggested. An early version of UNIFAC was published in 1975 but it soon became clear that a very substantial, systematic effort for data reduction was required to realize the full potential of the UNIFAC method. This effort was patiently carried out by Aage Fredenslund and Peter Rasmussen at Lyngby, Denmark, and by Jürgen Gmehling at Dortmund, Germany. As a result of their diligence and devotion, the UNIFAC method has now been significantly enlarged beyond its original scope.

As new data and additional experience become available, the utility and reliability of UNIFAC will increase. However, the present achievement of Fredenslund, Gmehling, and Rasmussen already covers a wide range of application in chemical industry. It is therefore a pleasure to welcome this monograph to the chemical design engineers and to congratulate the authors on having presented an important service toward successful design of separation equipment in chemical technology.

J.M. Prausnitz

February 1977

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CHAPTER 1

INTRODUCTION

A large part of chemical engineering design is concerned with separation processes. Many of these are diffusional operations of the phase-contacting type; distillation, absorption, and extraction are probably the most common. For rational design of such separation processes, we require quantitative information on the phase equilibria in the binary or multicomponent mixture under consideration.

The purpose of this book is to describe a method for predicting such quantitative information, the UNIFAC group-contribution method. In the course of the book we describe by extensive examples the quality of predictions. We give references to tested vapor-liquid equilibrium data on which the model is based, and finally examples of how UNIFAC may be used in practical engineering design calculations are listed. The computer programs associated with UNIFAC (testing phase equilibrium data, estimation of parameters, prediction of phase equilibria, and distillation calculations) are given in appendix. We hope the reader will find it easy to use and extend the UNIFAC method.

1.1 THE PHASE EQUILIBRIUM PROBLEM

Phase equilibrium thermodynamics serves as the mathematical framework for providing quantitative information on phase equilibria. Figure 1.1 illustrates schematically the problem (see [1]).

We are given a mixture with M components and two phases, and we suppose that the two phases have reached an equilibrium state. Equilibrium thermodynamics helps answer the following question: If we know the mole fractions in phase I ($x_1, x_2 .. x_M$)

and the temperature T, what are the mole fractions in phase II $(y_1, y_2 .. y_M)$ and the pressure P ?
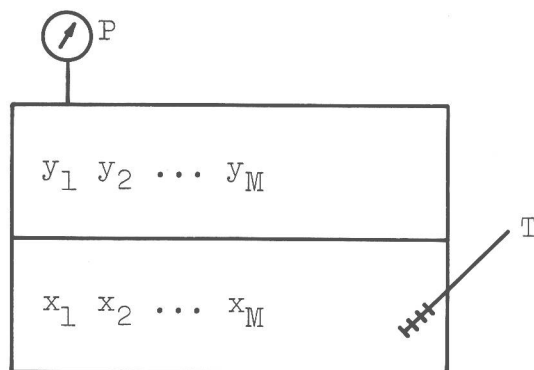
Figure 1.1

AN EQUILIBRIUM STAGE

For rational design of diffusional separation processes, this question must be answered, often with high degree of accuracy. Most diffusional separation processes contain many equilibrium stages in series. Therefore, and because the answer to the above question most often must be provided within an iterative procedure, the method of arriving at the answer must be relatively fast and simple.

To solve problems illustrated in Figure 1.1 we use the condition for phase equilibrium (see [1], p. 21):

$$f_i^I = f_i^{II} \qquad i = 1, 2, .. M \qquad (1.1)$$

where f_i is the fugacity of component i in phase I or II. There are M such relationships, where M is the total number of components in the mixture.

If phase I is vapor and II is liquid, Equation (1.1) is rewritten in terms of the vapor phase fugacity coefficient φ_i, the liquid phase activity coefficient γ_i, and the liquid phase reference fugacity f_i^o:

$$\varphi_i y_i P = \gamma_i x_i f_i^o \qquad i = 1, 2, .. M \qquad (1.2)$$

If both phases are liquid (mole fractions given by x_i^I and x_i^{II}), Equation (1.1) becomes

$$x_i^{\,I}\gamma_i^{\,I} = x_i^{\,II}\gamma_i^{\,II} \qquad i = 1, 2, \ldots M \qquad\qquad (1.3)$$

At pressures up to a few atmospheres, the fugacity coefficients and reference fugacities are readily calculated using the virial equation in conjunction with second virial coefficients obtained from experimental information or generalized correlations (see Chapter 2 of this book). Indeed, at these low pressures φ_i is often nearly unity and $f_i^{\,o}$ is often nearly the pure-component vapor pressure at the same temperature as the mixture. To answer the question stated in connection with the phase equilibrium problem we are then left with the problem of establishing a relation for the activity coefficients as functions of composition x_i and temperature T. The UNIFAC group-contribution method is a such relation.

1.2 ORIGIN AND RANGE OF APPLICABILITY OF THE UNIFAC METHOD

The UNIFAC method for calculation of activity coefficients [2] is based on the group-contribution concept, which has been successful for estimating a variety of pure-component properties such as liquid densities, heat capacities, and critical constants. The basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecules' functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids in terms of a much smaller number of parameters which characterize the contributions of individual groups. In addition, we obtain a technique for predicting phase equilibria in systems for which no data exist. It is for example within the framework of the group-contribution approach possible to predict the equilibrium compositions in all ketone-alkane mixtures from data on, say, acetone-cyclohexane.

Any group-contribution method is approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of a group-contribution method is additivity; the

contribution made by one group is assumed to be independent of that made by another group. This assumption is valid only when the influence of any one group in a molecule is not affected by the nature of other groups within that molecule.

For example, we would not expect the contribution of a C=O (carbonyl) group in a ketone (say, acetone) to be the same as that of a C=O group in an organic acid (say, acetic acid). On the other hand, experience suggests that the contribution of a C=O group in acetone is close to (although not identical with) the contribution of a C=O group in 2-butanone.

Accuracy of correlation improves with increasing distinction of groups; in considering, for example, aliphatic alcohols, in a first approximation no distinction is made between the position (primary or secondary) of a hydroxyl group, but in a second approximation such distinction might be desirable. In the limit, as more and more distinctions are made, we recover the ultimate group, namely, the molecule itself. In that event, the advantage of the group-contribution method is lost. For practical utility, a compromise must be attained. The number of distinct groups must remain small but not so small as to neglect significant effects of molecular structure on physical properties.

Extension of the group-contribution idea to mixtures is extremely attractive; since the number of pure fluids in chemical technology is already very large, the number of different mixtures is still larger, by many orders of magnitude. A large number of multicomponent liquid mixtures of interest in the chemical industry can be constituted from perhaps fifty functional groups.

In its present state of development, the UNIFAC method may be used to predict the phase equilibria in non-electrolyte mixtures for temperatures in the range of 300-425 K and pressures up to a few atmospheres. All components must be condensable. Precisely which groups are covered is given in Chapter 4. In addition to its predictive capabilities, the UNIFAC method today correlates more than 70% of the published vapor-liquid equilibrium data at pressures up to a few atmospheres.

The aim of the UNIFAC method is to provide an accurate and reliable method for predicting vapor-liquid equilibria. Therefore the present table of group-contribution parameters is where possible based on vapor-liquid equilibrium data only. The equations in the UNIFAC method may also be used to predict liquid-liquid equilibria and excess enthalpies. However, in the present development of the UNIFAC method, accurate prediction of these has been of second priority.

1.3 ORGANIZATION OF THE BOOK

This book is intended for the process design engineer who needs reliable predictions of phase equilibria for designing distillation columns and other separation processes. The aim of this book is to describe the UNIFAC group-contribution method for estimating activity coefficients and to provide a manual for the design engineer so that he may use it with confidence. This book does not contain detailed theoretical considerations - for this we refer the reader to [1].

Chapters 2 and 3 describe calculation of vapor and liquid phase nonidealities in terms of, respectively, fugacity and activity coefficients. The UNIFAC method is stated in Chapter 4, and Chapter 5 deals with the determination of UNIFAC parameters, i.e. the parameter estimation procedure used in establishing the parameters needed for the model. Prediction of binary and multicomponent vapor-liquid equilibria is shown for a large number of systems in Chapters 6 and 7, and the potential UNIFAC has for predicting liquid-liquid equilibria is illustrated in Chapter 8. Application of UNIFAC to practical distillation design problems is shown in Chapter 9.

Finally, the computer programs used in connection with the UNIFAC method are listed in Appendix.

REFERENCES

1. J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Englewood Cliffs, N.J., 1969.

2. Aage Fredenslund, R.L. Jones and J.M. Prausnitz, AIChE Journal 21(1975)1086.

CHAPTER 2

VAPOR PHASE NONIDEALITY

The condition for phase equilibrium was in Chapter 1 stated as:

$$f_i^V = f_i^L \qquad i = 1,2 \ .. \ M \tag{2.1}$$

where f_i is the fugacity of component i in the vapor (V) or liquid (L) phase.

For a mixture where the vapor phase is an ideal gas, one may write:

$$f_i^V = y_i P \tag{2.2}$$

where y_i is the mole fraction and P is the total pressure.

Nonideality in the vapor phase is characterized by the fugacity coefficient φ_i defined in (2.3):

$$f_i^V = \varphi_i y_i P \tag{2.3}$$

Except for mixtures containing strongly associating substances as organic acids, the value of φ_i will be close to unity at the low pressures considered in this book. Nevertheless we have wanted to be sure that all vapor phase nonidealities are taken into account in the calculations for the vapor phase and not carried over to the fugacities for the liquid phase. We have therefore calculated f_i^V by means of (2.3) in all our data reductions for parameter estimation in the UNIFAC model.

In this chapter we will discuss methods for calculating φ_i.

2.1 FUGACITY COEFFICIENTS FROM THE VIRIAL EQUATION

The fugacity coefficient can be calculated by means of
Equation (2.4). It is derived through a series of basic thermodynamic manipulations (see [1], p. 30):

$$\ln \varphi_i = \frac{1}{RT} \int_0^P (\bar{v}_i - \frac{RT}{P})dP \qquad\qquad (2.4)$$

P and T are the pressure and temperature for the system, R is
the universal gas constant, and $\bar{v}_i$ is the partial molar
volume of component i in the mixture.

The problem of finding φ_i has now been changed to the problem of finding $\bar{v}_i$ from an equation of state. One such
equation is the virial equation, which gives the compressibility factor of the mixture, z, as a function of composition,
temperature, and pressure or volume.

At pressures up to a few atmospheres the volume explicit
virial equation may be truncated after the second term:

$$z = \frac{Pv}{RT} = 1 + \frac{BP}{RT} \qquad i \text{ and } j = 1,2 .. M \qquad (2.5)$$

v is the molar volume of the mixture and B is the second virial
coefficient accounting for two molecules interacting.

In a mixture with M components we have

$$B = \overset{i}{\Sigma} \overset{j}{\Sigma} y_i y_j B_{ij} \qquad i \text{ and } j = 1,2 .. M \qquad (2.6)$$

The B_{ij}'s represent interactions between molecules i and
j. If i = j one has the virial coefficient B_{ii} for a pure
component.

Combination of equations (2.4), (2.5) and (2.6) gives:

$$\ln \varphi_i = \frac{P}{RT} (2 \overset{j}{\Sigma} y_j B_{ij} - B) \qquad j = 1,2 .. M \qquad (2.7)$$

It should be noted here that one very often finds a different expression for φ_i based on the virial equation comprising
only pair interactions [1]: