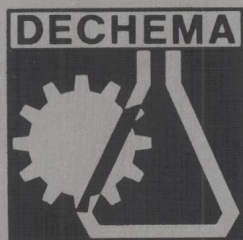J. Gmehling

U. Onken

VAPOR-LIQUID EQUILIBRIUM DATA COLLECTION

Aqueous-Organic Systems

DECHEMA

Chemistry Data Series

Vol. I, Part 1

J. Gmehling
U. Onken

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Vapor-Liquid Equilibrium
Data Collection
1

Tables and diagrams of data for binary and
multicomponent mixtures up to moderate pressures.
Constants of correlation equations for computer use.

J. Gmehling, U. Onken

Lehrstuhl Technische Chemie B
(Prof. Dr. U. Onken)
Universität Dortmund

PREFACE OF EDITORS

Thermophysical property data are needed for the designing of process units. In designing process units, one cannot rely on the data found in the literature alone: for example, one can seldom find data for mixtures. What one needs in modern plant design is the exactest possible advance computation of material data.

This was why the DECHEMA Engineering Data Committee recommended the establishment of a data bank for chemical engineering in 1973. Work on the Dechema Data Service (DSD) began during the same year. This data centre is to collect and store all thermophysical data of substances that are relevant to chemical engineering; above all, it must be able to evaluate them and carry out computations for planned applications.

In the meantime, the necessary programs have been purchased or are being developed. A program system for the computation of thermophysical data, the Thermophysical Properties Program Package of Messrs. Uhde of Dortmund, was first installed at the DECHEMA to compute the pure substance and mixture data on request of users. The introduction of the data analysis system (SDA) fulfilled the requisites to evaluating data and obtaining basic data. A data storage system that will accommodate any desired data and data quantities and the corresponding programs (data retrieval system, SDR) is being developed.

Since the beginning of 1977, the Dechema Data Bank and Service has formed part of the newly-established Technical Information Centre — Chemistry in Frankfurt which is sponsored by the Federal German Government.

It was soon found that the existing data computation methods were inadequate for many cases. The DECHEMA therefore invited the users of the data system to establish a development group which has been concerning itself with the development of new computation methods for thermophysical property data since then. A study entitled "Stoffdaten" which the DECHEMA Engineering Data Committee prepared on request of the Federal Minister for Research and Technology analyzes the data situation, particularly from the viewpoint of advance computation of thermophysical properties, and makes recommendations for future developments. This study will serve as the basis for all future development work.

We intend to publish the measured data, data evaluations and other data collections resulting from the development of methods as generally-available information in the DECHEMA Chemistry Data Series, which is published at irregular intervals.

The above-mentioned development work concentrates on computation methods for phase equilibria, in particular, vapor-liquid equilibria. In this field, the work of Prof. Onken and Dr. Gmehling in Dortmund which was supported by the DECHEMA has been very fruitful; in particular, it led to an extension of the UNIFAC method, which is at present being integrated into the data compiler. Prof. Onken and Dr. Gmehling have produced what is probably the largest collection of vapor-liquid equilibrium data that is today available with evaluation programs and experimental data — for direct retrieval by means of computers. This is also part of the DECHEMA Data Service and can be used by subscribers.

We present the evaluation of this material in several parts of the first volume of the new series. We hope that this gives particularly the users an instrument that will allow them to solve their problems consideralby more easily and quickly than before.

Frankfurt / Main, March 1977

Dieter Behrens
Reiner Eckermann

AUTHORS' PREFACE

Vapor-liquid equilibria form the basis of various kinds of chemical engineering calculations. In particular this is true for the design of certain separation processes, such as distillation and condensation. For the large number of computations of this kind vapor-liquid equilibrium data for the systems to be handled are required. Unfortunately experimental data are very often either incomplete or totally lacking. In principle the appropriate measurements are not too difficult to perform, but it can be very time-consuming to carry them out, especially for multicomponent systems, if values for numerous data points have to be obtained. With the existence of equations representing multicomponent liquid mixtures with binary parameters only, such as Wilson, NRTL and UNIQUAC, the amount of experimental work necessary to describe multicomponent systems has been reduced considerably; even so, equilibrium measurements often are not feasible because of lack of time, for instance, when process alternatives have to be evaluated, as happens in process development and in preliminary design. In those cases the missing binary parameters must be predicted. Regardless of the method employed for prediction, the results will be the more reliable, the more data for related systems have been used.

It was the intention of the senior author, when he took the Chair of Industrial Chemistry B at the new University of Dortmund in 1971 to employ the vast store of vapor-liquid equilibrium data published in literature for the prediction of binary parameters of liquid mixtures. The realisation of this plan became possible only when the junior author joined the group in 1973. A computerized compilation of binary and multicomponent vapor-liquid equilibria, now called Dortmund Data Bank (DDB), was started for the purpose of testing and developing prediction methods. At the suggestion of many colleagues and of DECHEMA and GVC we are now making this collection of VLE-data available to others. This has only been possible with the help of DECHEMA. In order to limit the price of this VLE-data collection, the print-out of DDB is used as basis for reproduction.

Since our work on prediction methods is aimed at non-electrolyte systems, this data collection is restricted mainly to mixtures of organic compounds, but does include water. Within this scope all VLE-data up to pressures of 15 bars have been collected from the available literature (handbooks, tables, scientific journals, etc.) and filed on magnetic tape. The printed edition of our data compilation will comprise all available data published up to 1975. Besides experimentally determined data points from the literature, values calculated by the following correlation equations are included in the tables: Margules, van Laar, Wilson, NRTL, UNIQUAC. The parameters for these equations are also tabulated, as are the constants of the Antoine vapor pressure equation for the pure compounds.

Wherever possible, the tables of data are accompanied by an equilibrium diagram from which the type of system can be perceived at first glance. The reliability of data is indicated by results of two different thermodynamic consistency tests. Parameter adjustment of the correlation equations has been achieved by the Nelder-Mead optimizing method. Deviations between measured and calculated data points and the resulting mean of absolute deviations give an idea of the quality of fit. Such values must be used with judgment, however. If for example for one set of data the mean deviations for two correlation equations are different, but both well below experimental error, this does not mean that the equation with the smaller deviation is necessarily the better one for all purposes. We can, of course, not give general recommendations here as to which correlation equation should be used; this has rather to be left to the judgment of the individual user, the optimal choice depending on the actual problem. In those cases, however, where some of the binary parameters in a multicomponent system are not available from experiment, but can be predicted by the UNIFAC-method, the obvious procedure will be to use the UNIQUAC-equation, since UNIFAC uses the same form of concentration dependence for the activity coefficient.

More detailed information on scope and most profitable use of our data collection is given under the heading "General Remarks and Explanations" at the beginning of Part 1, where also arrangement and organization of the tables are described.

We expect to add new data to our data bank as they appear and we plan to publish these data as supplements in the future. Therefore we are calling upon all workers in the field of vapor-liquid equilibrium to send us separate prints of new papers on their experimental results. We shall also be grateful to each user of the data collection who will notify us of mistakes or omissions in the tables.

V

PREFACE
by Prof. Prausnitz

Thermodynamic properties of liquid mixtures constitute one of the oldest fields of research in physical chemistry. The first issues of the "Zeitschrift für physikalische Chemie", about 90 years ago, devoted a large fraction of their pages to experimental and theoretical studies on the equilibrium properties of liquid solutions. This subject has fascinated numerous outstanding scientists and the number of published articles dealing with it has reached many thousands.

Despite the tremendous effort which has been expended toward gaining a truly fundamental understanding of liquid mixtures, our present state of knowledge is far from satisfactory. We are still in the early stages of formulating an adequate theory of the pure liquid state and in a very early stage of extending that theory to mixtures. Our inadequate knowledge is unfortunate not only from a scientific point of view but even more from the viewpoint of technology. Liquid mixtures are commonly found in numerous chemical and related industries including those concerned with polymers, pharmaceuticals, coal, gas, petroleum and other natural resources. Efficient processing of such mixtures requires a quantitative understanding of their equilibrium properties. Physically meaningful correlation of these properties is the task of molecular thermodynamics.

To make progress in efficient engineering and in the practical applications of molecular thermodynamics, it is necessary that those properties which have been studied experimentally be made readily available to scientists and engineers in industry and research. Since the literature reporting experimental results is both large and widely dispersed, it is a formidable effort to collect it in one convenient place. A magnificent start in this effort has now been made by Professor U. Onken and Dr. J. Gmehling. Not only have they collected a large body of phase-equilibrium data but, in addition, they have reduced these data such that their representation in suitable mathematical form is directly useful to the chemical design engineer. Through mathematical representation, the experimental data can be systematically interpolated and, with caution, extrapolated to new conditions of temperature, pressure and composition. Mathematical representation of binary systems, therefore, not only extends the range of the experimental work but, using suitable models and aided by electronic computers, enables the chemical engineer to predict multicomponent phase equilibria, as required in typical industrial operations.

It is evident that Professor Onken and Dr. Gmehling have provided an extremely valuable service to those chemists and chemical engineers who are in academic research or in industrial practice. The chemical profession heartily welcomes this first volume in a series of useful publications. It is a pleasure to congratulate the authors on completing the first part of their important mission and to thank them for their patience, diligence and devotion.

J. M. Prausnitz
University of California
Berkeley

LIST OF SYMBOLS

A	constant in Antoine vapor pressure equation (70)
A'	area above x-axis in area test, eq. (52)
A_D	constant in equation (22) for dimerization
A_{ij}	parameters in the equations of Margules (28) and van Laar (29)
a_k	coefficient for Legendre polynomial of the order k
B	constant of Antoine vapor pressure equation (70)
B'	area below x-axis in area test, eq. (52)
B_D	constant in equation (22) for dimerization
C	constant of Antoine vapor pressure equation (70)
D	see eq. (52)
f_i	fugacity of component i
ΔG	change in molar Gibbs energy G by mixing
G_{ij}	expression in NRTL equation (31, 37), see footnote [2] of Table 1
g	see eq. (56)
g'	see eq. (57)
g_{ij}	interaction parameter in NRTL equation (31, 37)
ΔH	molar enthalpy of mixing
J	see eq. (53)
K_D	equilibrium constant of dimerization, eq. (16)
L_k	Legendre polynomial of the order k
l_i	see eq. (35)
n	number of moles
P	total pressure
p_i	partial pressure
p_i^0	vapor pressure of pure component i
q_i	area parameter of component i in UNIQUAC equation (32-35, 38-40)
R	gas constant
r_i	volume parameter of component i in UNIQUAC equation (32-35, 38-40)
T	absolute temperature in kelvins
t	temperature in degrees Celsius
u_{ij}	interaction parameter in UNIQUAC equation (32-35, 38-40)
V	molar volume
ΔV	molar excess volume of mixing
V_i	partial molar volume of component i
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
z	coordination number; in UNIQUAC equation (32-35, 38-40) $z = 10$
α	nonrandomness parameter in NRTL equation (31, 37)
γ_i	activity coefficient of component i
φ_i	volume fraction of component i (see Table 2)
Λ_{ij}	parameter in Wilson equation (30, 36)
λ_{ij}	interaction energy in Wilson equation (30, 36)

μ_i	chemical potential of component i
τ_{ij}	parameter in NRTL equation (31, 37), see footnote [2]) of Table 1; parameter in UNIQUAC equation (32-35, 38-40), see Table 4 (note that τ_{ij} has a different meaning in NRTL and UNIQUAC equations)
Φ_i	fugacity coefficient of component i
ϑ_i	area fraction of component i
ln	natural logarithm
log	common logarithm (base 10)

Superscripts

E	for excess quantity, e.g. $\triangle G^E$
G	gas or vapor phase
id	ideal
L	liquid phase
0	pure component
∞	infinite dilution
', '', '''	phase I, II, III

Subscripts

calc	calculated
exp	experimental
D	dimer; also dimerization
i, j, k, l, m	component i, j, k, l, m
M	monomer
n	data point
rel	relative

GENERAL REMARKS AND EXPLANATIONS

1. INTRODUCTION

With these general remarks and explanations we provide information we believe to be necessary for the correct use of the data collection. In this general part the following subjects will be treated:
1. Equations from thermodynamics
2. Computer processing of vapor-liquid equilibrium data
3. Explanations and recommendations for using the tables

The section on thermodynamic equations is not to be regarded as a substitute for a textbook on thermodynamics of vapor-liquid equilibrium; it is rather intended to present the equations used for data correlation in order to state definitions, assumptions, and limits of validity.

2. EQUATIONS FROM THERMODYNAMICS

2.1. Vapor-Liquid Equilibrium

Equilibrium between phases (I, II, III ...) in a multicomponent system means that temperature T, pressure P and the chemical potential μ of each component i must be the same in all phases:

$$T' = T'' = T''' = \ldots\ldots \tag{1}$$

$$P' = P'' = P''' = \ldots\ldots \tag{2}$$

$$\mu_i' = \mu_i'' = \mu_i''' = \ldots\ldots \; (i = 1, 2, \ldots m) \tag{3}$$

For the discussion of phase equilibria the conditions of equation (3) can be expressed in terms of fugacities f, e.g.

$$f_i' = f_i'' = f_i''' = \ldots\ldots \; (i = 1, 2, \ldots m) \tag{4}$$

In the case of vapor-liquid equilibrium we obtain for component i

$$f_i^G = f_i^L \tag{5}$$

The concentration dependence of the vapor phase fugacitiy f_i^G is given by

$$f_i^G = y_i \Phi_i P \tag{6}$$

Since by definition the fugacity of an ideal gas is equal to its pressure, the fugacity coefficient Φ_i approaches unity for very low pressures:

$$\lim_{(P \to 0)} \Phi_i = 1 \tag{7}$$

Φ_i is related to pressure by

$$\Phi_i = \exp\left(\frac{1}{RT} \cdot \int_0^P (V_i^G - \frac{RT}{P}) \, dP\right) \tag{8}$$

This equation is the starting point for calculations of the fugacity coefficients Φ_i. The necessary data for the partial molar volumes V_i^G in the gas phase are determined from equations of state. For moderate pressures (up to 10-20 bars) this can be done through the second virial coefficients; a method for their calculation, also with mixtures of polar compounds, has recently been described by Hayden and O'Connell [7]. For higher pressures other equations of state, such as the Redlich-Kwong equation [21] (two parameters), are used.

The liquid phase fugacity f_i^L of component i is related to its mole fraction x_i in the liquid phase by

$$f_i^L = x_i \gamma_i f_i^{0\,L} \tag{9}$$

Here γ_i is the liquid phase activity coefficient of component i; it is a function of temperature, pressure and composition. $f_i^{0\,L}$ is the fugacity of liquid i at system temperature and pressure at a defined standard state. With vapor-liquid equilibrium the standard state is nearly always the pure component at the temperature and the pressure of the mixture. With this choice of standard state it follows that

$$\text{for } x_i = 1: \quad f_i^L = f_i^{0\,L} \tag{10a}$$

$$\text{and} \quad \gamma_i = 1 \tag{10b}$$

The fugacity f_i^{0L} of the pure liquid is related to its vapor pressure p_i^0:

$$f_i^{0L} = p_i^0 \cdot \Phi_i^0 \cdot \exp\left(\frac{1}{RT} \cdot \int_{p_i^0}^P V_i^L \, dP\right) \tag{11}$$

Here the expression $\exp\left(\frac{1}{RT} \cdot \int_{p_i^0}^P V_i^L \, dP\right)$ is the so-called Poynting correction which allows for the influence of the change of pressure on fugacity from P to p_i^0. Φ_i^0 is the fugacity coefficient for the pure component at the pressure p_i^0; it is given by

$$\Phi_i^0 = \exp\left(\frac{1}{RT} \cdot \int_0^{p_i^0} (V_i^G - \frac{RT}{P})\ dP\right) \tag{12}$$

By combining equations (5), (6), (9) and (11) one obtains the following equation for equilibrium between vapor and liquid at the temperature T and the pressure P:

$$y_i \bullet \Phi_i \bullet P = x_i \cdot \gamma_i \cdot p_i^0 \cdot \Phi_i^0 \cdot \exp\left(\frac{1}{RT} \int_{p_i^0}^{P} V_i^L\ dP\right) \tag{13}$$

At low pressures (up to a few bars) equation (13) can be simplified, because the fugacity coefficients nearly cancel each other and Poynting corrections usually are very close to unity. Neglecting these corrections leads to

$$y_i \cdot P = x_i \cdot \gamma_i \cdot p_i^0 \tag{14}$$

This is the equation used in preparation of the tables, except for systems containing carboxylic acids. Note that for an ideal system all γ_i are equal to unity at any composition, and equation (14) then reduces to Raoult's law:

$$y_i \cdot P = x_i \cdot p_i^0 \tag{15}$$

For systems with components associating in the vapor phase, deviations from ideal gas behavior must be accounted for even at low pressures. As has been shown by Marek [13, 14], this can be done by regarding vapor phase association as a chemical equilibrium reaction, for which equilibrium constants can be defined. The new species formed by association, e.g. dimers, trimers etc., are treated as individual components of the vapor phase, whereas the liquid phase is regarded as being composed of the monomers only. For a binary system in which one component forms dimers in the vapor phase but no other associates, the following relations hold with component 1 as associating component:

$$K_D = \frac{p_{1D}}{p_{1M}^2} \tag{16}$$

K_D equilibrium constant of dimerization

p_{1M} partial pressure of monomer

p_{1D} partial pressure of dimer

$$P = p_{1M} + p_{1D} + p_2 \tag{17}$$

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$$y_1 = \frac{p_{1M} + 2p_{1D}}{P} \qquad (18)$$

$$p_{1M} = x_1 \cdot \gamma_1 \cdot p_{1M}^0 \qquad (19)$$

$$p_2 = x_2 \cdot \gamma_2 \cdot p_2^0 \qquad (20)$$

Equations (19) and (20) imply that all liquid-phase nonidealities including association are lumped into the two activity coefficients γ_1 and γ_2. p_{1M}^0 is the hypothetical vapor pressure of the pure monomer of component 1; it is related to the real vapor pressure p_1^0 of pure component 1:

$$p_1^0 = p_{1M}^0 + K_D (p_{1M}^0)^2 \qquad (21)$$

Equation (21) is obtained by combining equations (16), (17) and (18) for $y_1 = 1$.

The temperature dependence of dimerization constants K_D can be expressed by

$$K_D = A_D + \frac{B_D}{T} \qquad (22)$$

Values of A_D and B_D for the calculation of K_D are listed in Appendix B.

Equations (16) to (22) are used in the tables to describe vapor phase non-idealities of carboxylic acids; thus only dimerization is considered.

2.2. Correlation of Liquid-Phase Activity Coefficients

Use of equation (14) for nonideal systems means that nonideal behavior is described solely by liquid-phase activity coefficients. These are functions not only of temperature, but in particular of composition. Therefore equations for the concentration dependence of liquid-phase acivity coefficients are required. In a given system these are not independent from one another, but are coupled by the Gibbs-Duhem equation. Therefore it is practical and also logical to start from a single original function, such that this equation is satisfied. For the purpose of describing nonideal behavior of mixtures the excess functions are defined as the difference between thermodynamic functions of a real mixture and those of an ideal mixture at the same conditions of temperature, pressure, and composition. Accordingly the molar excess Gibbs energy of mixing ΔG^E is given by

$$\Delta G^E = \Delta G - \Delta G^{id} \qquad (23)$$

With the symbol Δ designating the change in G resulting from the mixing process, and the superscript id referring to an ideal mixture, ΔG^E is related

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