

(130 °C)

(117) BENZENE (1) - CYCLOHEXANE (2) - N-HEXANE

# physical sciences data 3

## prediction of vapor-liquid equilibria by the asog method

k. kojima and k. tochigi

kodansha ltd.  
tokyo

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Vol. 1 J. Wisniak and A. Tamir, Mixing and Excess Thermodynamic Properties

Vol. 2 J.R. Green and D. Margerison, Statistical Treatment of Experimental Data

## Preface

This monograph deals with prediction of vapor-liquid equilibria by the group contribution method referred to as the Analytical Solutions of Groups (ASOG). Vapor-liquid equilibrium is an essential property on which the development and design of distillation processes are based, and because of this important practical application, many attempts have been made to predict vapor-liquid equilibria. At present the trend is to use binary data for predicting the vapor-liquid equilibria of multicomponent systems. However, from a practical standpoint, it is more important to develop a method which will use binary data to predict the vapor-liquid equilibria of both multicomponent systems and binary systems at the same time. For this purpose the group contribution method is considered to be a very useful approach because it takes into account the groups making up a liquid solution in order to predict the activity coefficients of the components in the solution.

Over the last few years we have studied the prediction of vapor-liquid equilibria by the Analytical Solutions of Groups (ASOG). We have determined, for 31 groups, the group pair parameters necessary for predicting activity coefficients, and we have used these parameters to predict the vapor-liquid equilibria for about 1100 systems at low pressures. Our findings confirmed that the absolute arithmetic deviation for a vapor composition is 1.2%. This monograph describes these results in detail. It discusses the theory of vapor-liquid equilibria, together with the fundamental equations in ASOG, and the method for predicting vapor-liquid equilibria. Tables provide the values of the group pair parameters for the 31 groups and the predicted values of vapor-liquid equilibria for about 1100 systems. We hope this monograph will prove useful to chemical engineers engaged in the development and design of separation processes.

February 1979

K. Kojima  
K. Tochigi

## Nomenclature

$A, B, C$	Antoine vapor pressure constants
$a_{kl}$	group interaction parameter in ASOG
$f_i$	fugacity of component $i$
$K$	vapor-phase equilibrium constant for dimerization
$m_{kl}, n_{kl}$	group pair parameters in ASOG
$P$	total pressure
$P_i^s$	vapor pressure of pure liquid $i$
$X_k$	group fraction of group $k$
$x_i$	mole fraction of component $i$ in liquid phase
$y_i$	mole fraction of component $i$ in vapor phase
$\Gamma_k$	group activity coefficient of group $k$
$\Gamma_k^{(i)}$	group activity coefficient of group $k$ at standard state (pure component $i$ )
$\gamma_i$	activity coefficient of component $i$
$\eta$	true mole fraction in vapor phase
$\eta_{A_1}^\circ$	true mole fraction of monomer $A_1$ in saturated vapor of pure liquid $A$
$\eta_{B_1}^\circ$	true mole fraction of monomer $B_1$ in saturated vapor of pure liquid $B$
$v_i^{FH}$	number of atoms (other than hydrogen atoms) in molecule $i$
$v_{ki}$	number of atoms (other than hydrogen atoms) in group $k$ in molecule $i$
$\varphi_i$	fugacity coefficient of component $i$

### <Superscripts>

$FH$	size contribution
$G$	group contribution
$(i)$	standard state
$L$	liquid phase
$s$	saturation
$V$	vapor phase
I, II	liquid phases I, II
$^\circ$	pure substance

### <Subscripts>

$A, B$	molecule $A$ and $B$
$A_1, B_1$	monomers of components $A, B$
$A_2, B_2$	dimers of components $A, B$

$i, j$	molecule $i$ and $j$
$i1$	monomer of component $i$
$i2$	dimer of component $i$
$i1, j1$	cross dimer of components $i, j$
$k, l, m$	group $k, l$ and $m$
$ki$	group $k$ in molecule $i$
$1, 2, 3, \dots, N$	component $1, 2, 3, \dots, N$



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## Chapter One

### Vapor-Liquid Equilibria

#### 1.1 NON-IDEAL HOMOGENEOUS SYSTEMS

The criterion of vapor-liquid equilibrium for each component in an  $N$  component system is given by

$$\begin{aligned} f_i^V & \text{ (fugacity of component } i \text{ in the vapor phase)} \\ &= f_i^L \text{ (fugacity of component } i \text{ in the liquid phase)} \\ & \quad i = 1, 2, \dots, N \end{aligned} \quad (1.1)$$

where  $f$  represents fugacity, and superscripts  $V$  and  $L$  refer respectively, to the vapor and the liquid phase. Subscript  $i$  indicates component  $i$  in the mixture.

This monograph is concerned with low pressures of less than one atmosphere in which the vapor phase can be treated as an almost-ideal gas. Assuming that the vapor phase follows the ideal gas law, the fugacity of component  $i$  in the vapor phase is given by

$$f_i^V = Py_i \quad (1.2)$$

where  $y_i$  is the mole fraction of component  $i$  in the vapor phase, and  $P$  is the total pressure.

The fugacity of component  $i$  in a non-ideal liquid solution is given, at low pressures, by

$$f_i^L = \gamma_i x_i P_i^s \quad (1.3)$$

where  $x_i$  is the mole fraction and  $\gamma_i$  is the activity coefficient of component  $i$  in the liquid phase, and  $P_i^s$  is the vapor pressure of pure liquid  $i$ .

Substituting Eqs. (1.2) and (1.3) into Eq. (1.1), the vapor-liquid equilibrium for a non-ideal homogeneous system at low pressures becomes

$$Py_i = \gamma_i x_i P_i^s \quad i = 1, 2, \dots, N. \quad (1.4)$$

The activity coefficient for a component in a non-ideal liquid solution can be cal-

culated by knowing both the vapor and liquid phase compositions, the equilibrium pressure, and the temperature. The vapor-liquid equilibrium can then be calculated by expressing the activity coefficient as a function of the liquid composition.

## 1.2 HETEROGENEOUS SYSTEMS

Systems showing large deviations from the ideal liquid solution (eg., *n*-butanol-water, ethyl methyl ketone-water) are heterogeneous systems with two liquid phases in vapor-liquid equilibria. The criterion of vapor-liquid-liquid equilibrium for an *N* component system is given by

$$\begin{aligned} f_i^V & \text{ (fugacity of component } i \text{ in the vapor phase)} \\ & = f_i^I \text{ (fugacity of component } i \text{ in liquid phase I)} \\ & = f_i^{II} \text{ (fugacity of component } i \text{ in liquid phase II)} \\ & \quad i = 1, 2, \dots, N \end{aligned} \quad (1.5)$$

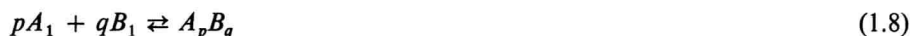
where superscript *V* refers to the vapor phase, and I, II to liquid phases I, II. Substituting Eqs. (1.2) and (1.3) into Eq. (1.5), the vapor-liquid equilibrium is given by

$$Py_i = \gamma_i^I x_i^I P_i^s = \gamma_i^{II} x_i^{II} P_i^s \quad i = 1, 2, \dots, N \quad (1.6)$$

where  $x_i^I, x_i^{II}$  are the mole fractions and  $\gamma_i^I, \gamma_i^{II}$  are the activity coefficients of component *i* in the two liquid phases I and II, respectively.

## 1.3 VAPOR-PHASE ASSOCIATION

Because systems containing carboxylic acids, such as acetic acid and propionic acid, contain associating components, the fugacity of components in the vapor phase cannot be obtained by Eq. (1.2), even at low pressures, and must be derived from chemical theory. Let us assume that a binary system consists of components *A* and *B*, and that the components give rise to the following associations and solvation (cross-association):



where  $A_1, B_1$  are the monomers,  $A_p$  and  $B_p$  are the *p*-mers, and  $A_p B_q$  is the (*p* + *q*) complex of components *A, B*. Also, assuming that the associating gases are in thermodynamic equilibrium, Eq. (1.9) has been derived by Prigogine and Defay.<sup>1)</sup>

$$f_A^V = f_{A_1}^V, \quad f_B^V = f_{B_1}^V \quad (1.9)$$

where  $f_A^V, f_B^V$  are the fugacities of components  $A, B$ , and  $f_{A_1}^V, f_{B_1}^V$  those of monomers  $A_1, B_1$  in the vapor phase.

Fugacities of monomers in the vapor phase are given by the following equations of Marek and Standart<sup>2)</sup> and of Nothnagel *et al.*<sup>3)</sup>

$$f_{A_1}^V = P\varphi_{A_1}\eta_{A_1}, \quad f_{B_1}^V = P\varphi_{B_1}\eta_{B_1} \quad (1.10)$$

where  $\varphi_{A_1}, \varphi_{B_1}$  are the fugacity coefficients and  $\eta_{A_1}, \eta_{B_1}$  are the true mole fractions of monomers  $A_1, B_1$  in the vapor phase. Assuming that  $\varphi_{A_1} = \varphi_{B_1} = 1$  at low pressures, Eq. (1.10) can be re-written as

$$f_{A_1}^V = P\eta_{A_1}, \quad f_{B_1}^V = P\eta_{B_1}. \quad (1.11)$$

The fugacity of component  $A$  in the liquid phase is given by

$$f_A^L = \gamma_A x_A \varphi_A^s P_A^s \exp[v_A(P - P_A^s)/RT]. \quad (1.12)$$

A similar equation may also be obtained for component  $B$ . In Eq. (1.12),  $\varphi_A^s$  is the fugacity coefficient of component  $A$  at vapor pressure  $P_A^s$  and temperature  $T$ , while  $v_A$  is the liquid molar volume of pure liquid  $A$ . Then, assuming that  $\exp[v_A(P - P_A^s)/RT] \div 1$  and  $\varphi_A^s \equiv f_A^s/P_A^s = f_{A_1}^s/P_A^s = \varphi_{A_1}^s P_A^s \eta_{A_1}^s / P_A^s = \varphi_{A_1}^s \eta_{A_1}^s \div \eta_{A_1}^s$ , Eq. (1.13) derives from Eq. (1.12) for component  $A$ . Similarly, the following equation is given for component  $B$ :

$$f_A^L = \gamma_A \eta_{A_1}^s P_A^s x_A, \quad f_B^L = \gamma_B \eta_{B_1}^s P_B^s x_B \quad (1.13)$$

where  $\eta_{A_1}^s, \eta_{B_1}^s$  represent the true mole fractions of monomers  $A_1, B_1$  in the saturated vapors of pure liquids  $A, B$ .

The condition for vapor-liquid equilibrium is given as  $f_A^V = f_A^L, f_B^V = f_B^L$  by Eq. (1.1). Combining these relations with Eq. (1.9), the condition of vapor-liquid equilibrium for a system containing vapor-associating components is given by

$$f_{A_1}^V = f_A^L, \quad f_{B_1}^V = f_B^L. \quad (1.14)$$

Therefore, substituting Eqs. (1.11) and (1.13) into Eq. (1.14), the vapor-liquid equilibrium for a system containing vapor-associating components is given by

$$P\eta_{A_1} = \gamma_A \eta_{A_1}^s P_A^s x_A, \quad P\eta_{B_1} = \gamma_B \eta_{B_1}^s P_B^s x_B. \quad (1.15)$$

The true mole fractions can be obtained for associating substances in the vapor phase by means of the associating-equilibrium equations coupled with the concept of material balance. The problem with the calculation is the necessity to consider the number of associations that may arise. We will consider dimerization association or solvation here as it has been pointed out<sup>4)</sup> that the formation of trimers or higher aggregates has little influence on the calculations.

Applying Eqs. (1.7) and (1.8) for dimerization association and solvation, and defining the equilibrium constant as  $K$ , we obtain

$$K_A = \eta_{A_2}/P\eta_{A_1}^2, \quad K_B = \eta_{B_2}/P\eta_{B_1}^2 \quad (1.16)$$

$$K_{AB} = \eta_{A_1, B_1}/P\eta_{A_1}\eta_{B_1} \quad (1.17)$$

where  $K_A$ ,  $K_B$  are the equilibrium constants for the associations shown in Eq. (1.7), and  $K_{AB}$  is the equilibrium constant for the solvation shown in Eq. (1.8). Also,  $\eta_{A_2}$ ,  $\eta_{B_2}$ ,  $\eta_{A_1, B_1}$  are the true mole fractions of dimers  $A_2$ ,  $B_2$ ,  $A_1 B_1$ . As the sum of true mole fractions in the vapor phase is 1, the following equation is satisfied:

$$\eta_{A_1} + \eta_{A_2} + \eta_{A_1, B_1} + \eta_{B_1} + \eta_{B_2} = 1. \quad (1.18)$$

Next, in order to calculate the true mole fraction  $\eta_{A_1}^\circ$  in Eq. (1.13) for monomer  $A_1$  in the saturated vapor of pure substance  $A$ , we first determine the equilibrium at vapor pressure  $P_A^s$  corresponding to temperature  $T$  as given by

$$K_A = \eta_{A_2}^\circ/P_A^s\eta_{A_1}^{\circ 2}, \quad \eta_{A_1}^\circ + \eta_{A_2}^\circ = 1 \quad (1.19)$$

where  $\eta_{A_1}^\circ$  may be calculated by applying Eq. (1.20). Similarly, the true mole fraction  $\eta_{B_1}^\circ$  of monomer  $B_1$  is given by Eq. (1.20).

$$\eta_{A_1}^\circ = \frac{-1 + \sqrt{1 + 4K_A P_A^s}}{2K_A P_A^s}, \quad \eta_{B_1}^\circ = \frac{-1 + \sqrt{1 + 4K_B P_B^s}}{2K_B P_B^s}. \quad (1.20)$$

Thus,  $\eta_{A_1}$ ,  $\eta_{B_1}$  can be evaluated from Eqs. (1.15) and (1.20), and  $\eta_{A_2}$ ,  $\eta_{B_2}$ ,  $\eta_{A_1, B_1}$  from Eqs. (1.16) and (1.17), using the dimerization equilibrium constants  $K_A$ ,  $K_B$ ,  $K_{AB}$ . The true mole fractions so obtained must satisfy Eq. (1.18).

By using the true mole fractions, the stoichiometric vapor mole fractions of components  $A$  and  $B$  in equilibrium with liquid compositions  $x_A$  and  $x_B$  may be obtained from Eq. (1.21).

$$y_A = \frac{\eta_{A_1} + 2\eta_{A_2} + \eta_{A_1, B_1}}{\eta_{A_1} + 2\eta_{A_2} + 2\eta_{A_1, B_1} + \eta_{B_1} + 2\eta_{B_2}}, \quad (1.21)$$

$$y_B = \frac{\eta_{B_1} + 2\eta_{B_2} + \eta_{A_1, B_1}}{\eta_{A_1} + 2\eta_{A_2} + 2\eta_{A_1, B_1} + \eta_{B_1} + 2\eta_{B_2}}.$$

Values of the dimerization equilibrium constants necessary for the calculations are given below for some carboxylic acids:

Formic acid	$\log K = -10.743 + 3083.0/T \text{ (323K} \sim 423\text{K)}^5$
Acetic acid	$\log K = -10.931 + 3347.0/T \text{ (323K} \sim 423\text{K)}^6$
Propionic acid	$\log K = -10.834 + 3316.0/T \text{ (323K} \sim 423\text{K)}^5$

Where the observed dimerization equilibrium constant is not available, the equilibrium constant for association can be predicted by applying Hayden and O'Connell's method.<sup>7)</sup> The equilibrium constant  $K_{AB}$  for solvation is calculated by using the relation  $K_{AB} = 2\sqrt{K_A K_B}$  appearing in Prausnitz' work.<sup>8)</sup>

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## Chapter Two

### Liquid-Phase Activity Coefficients

#### 2.1 ACTIVITY COEFFICIENT EQUATIONS

The liquid-phase activity coefficient is the most important requirement for vapor-liquid equilibrium calculations, which describe the activity coefficient as a function of liquid composition. Many studies have been undertaken in the past to determine the dependence of the activity coefficient on liquid composition. Important activity coefficient equations appear in the work of Prausnitz,<sup>1)</sup> Null,<sup>2)</sup> and Hála *et al.*<sup>3)</sup> In the following we will consider the Wilson,<sup>4)</sup> NRTL,<sup>5)</sup> and UNIQUAC<sup>6)</sup> equations published since 1964. Each of these allows the prediction of multicomponent activity coefficients from binary data alone.

*The Wilson equation.* In this activity coefficient equation applicable to homogeneous systems, the activity coefficient of component  $i$  in an  $N$  component system is given by

$$\ln \gamma_i = -\ln \left[ \sum_{j=1}^N x_j \Lambda_{ij} \right] + 1 - \sum_{k=1}^N \left[ \frac{x_k \Lambda_{ki}}{\sum_{j=1}^N x_j \Lambda_{kj}} \right] \quad (2.1)$$

where

$$\Lambda_{ij} \equiv \frac{v_j}{v_i} \exp \left[ -\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (\lambda_{ij} = \lambda_{ji}). \quad (2.2)$$

In Eq. (2.2),  $(\lambda_{ij} - \lambda_{ii})$  and  $(\lambda_{ij} - \lambda_{jj})$  are two Wilson parameters characteristic of the components  $i$  and  $j$ , obtainable from binary data. The parameters  $(\lambda_{ij} - \lambda_{ii})$  are assumed to be independent of temperature over a narrow temperature range.  $V_j$  is the liquid molar volume of pure component  $j$ .

*The NRTL (Non-Random, Two-Liquid) equation.* This activity coefficient equation is applicable to both heterogeneous and homogeneous systems. The activity coefficient of component  $i$  in an  $N$  component system is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^N \tau_{ji} G_{ji} x_j}{\sum_{l=1}^N G_{li} x_l} + \sum_{j=1}^N \left[ \frac{x_j G_{ij}}{\sum_{l=1}^N G_{lj} x_l} \left( \tau_{ij} - \frac{\sum_{r=1}^N x_r \tau_{rj} G_{rj}}{\sum_{l=1}^N G_{lj} x_l} \right) \right] \quad (2.3)$$



where

$$\tau_{ji} \equiv (g_{ji} - g_{ii})/RT \quad (g_{ji} = g_{ij}), \quad (2.4)$$

$$G_{ji} \equiv \exp(-\alpha_{ji}\tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij}). \quad (2.5)$$

In Eq. (2.4),  $(g_{ji} - g_{ii})$  and  $(g_{ji} - g_{jj})$  are two NRTL parameters (equivalent to Wilson parameters) characteristic of the components  $i$  and  $j$ . In Eq. (2.5),  $\alpha_{ji}$  is a third parameter, a constant varying roughly between 0.2 and 0.47 according to the type of system concerned.

*The UNIQUAC (Universal Quasi Chemical) equation.* In this activity coefficient equation, applicable to both heterogeneous and homogeneous systems, the activity coefficient of component  $i$  in an  $N$  component system is given by

$$\begin{aligned} \ln \gamma_i = & \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^N x_j l_j \\ & + q_i \left[ 1 - \ln \left( \sum_{j=1}^N \theta_j \tau_{ji} \right) - \sum_{j=1}^N \frac{\theta_j \tau_{ij}}{\sum_{k=1}^N \theta_k \tau_{ki}} \right] \end{aligned} \quad (2.6)$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1), \quad z = 10 \quad (2.7)$$

$$\theta_i = q_i x_i / \sum_{j=1}^N q_j x_j, \quad \phi_i = r_i x_i / \sum_{j=1}^N r_j x_j, \quad (2.8)$$

$$\tau_{ji} \equiv \exp \left[ -\frac{(u_{ji} - u_{ii})}{RT} \right] \quad (u_{ji} = u_{ij}). \quad (2.9)$$

In Eq. (2.9),  $(u_{ji} - u_{ii})$  and  $(u_{ji} - u_{jj})$  are two parameters characteristic of the components  $i$  and  $j$  that can be obtained from binary data. In Eq. (2.8),  $\theta_i$  is the area fraction and  $\phi_i$  the segment fraction;  $r_i$  and  $q_i$  are measures of, respectively, molecular van der Waals volumes and molecular surface and are constants for a pure component.

The binary parameters necessary for predicting vapor-liquid equilibria by the three activity coefficient equations discussed above appear in the following references:

Wilson [7, 8, 9, 10, 11]

NRTL [7, 10, 12]

UNIQUAC [6, 7].

Commonly,  $N(N - 1)$  parameters are necessary for predicting the vapor-liquid equilibria for an  $N$  component system if the equation used is like the Wilson, NRTL, and UNIQUAC equations, which contain just the parameters characteristic of a binary system and which predict the vapor-liquid equilibrium of multicomponent systems only from binary data. As  $N(N - 1)/2$  binary data are needed to determine these