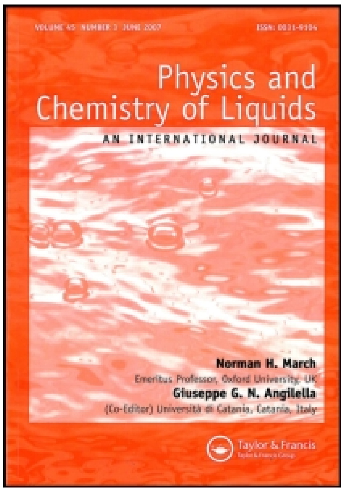

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ON THE GOTHARD MODEL FOR PREDICTING PHASE EQUILIBRIA

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The important features of the Gothard model are discussed and simple procedures are proposed for calculating the adjustable parameters of the model. The possibilities of the model for predicting phase separation are analyzed.

KEY WORDS: Activity coefficients, phase separation.

Gothard (1981, 1985) has proposed a new model for describing the behavior of real mixtures where the excess of Gibbs energy of the mixture is derived on the assumption that the largest contribution to deviation from ideal behavior is the result of a process governed by the mass action law and that there are groups of n neighbor molecules whose interactions determine the nonideality of the mixture. Gothard tested his model on 168 binary systems and 6 ternaries and claimed that it improved significantly the correlation of vapor-liquid equilibrium data in comparison with the results given by the Wilson and Renon equations.

The purpose of this communication is to analyze the most significant features of this model as well as suggest a simple method for calculating its parameters.

According to Gothard (1985)

$$\frac{G^E}{RT} = \frac{1}{\mathrm{K}} \ln\left[\frac{n(n-1)}{2}\right] \tag{1}$$

where

$$\frac{2}{n} = \sum_i \frac{x_i}{\sum_j n_{ij} x_j} \tag{2}$$

where x_i is the mole fraction of component i, n_{ij} are the adjustable parameters for the model and K is an additional parameter that equals four for systems without miscibility gaps.

For a binary system we get

$$\frac{2}{n} = \frac{x_1}{x_1 + x_2 n_{12}} + \frac{x_2}{x_2 + x_1 n_{21}} \tag{3}$$

and

$$\ln \gamma_1 = \frac{1}{K}\ln\left[\frac{n(n-1)}{2}\right] - \frac{x_2 n(2n-1)}{2K(n-1)}\left[\frac{n_{12}}{(x_1+x_2n_{12})^2} - \frac{n_{21}}{(x_2+x_1n_{21})^2}\right] \tag{4}$$

$$\ln \gamma_2 = \frac{1}{K}\ln\left[\frac{n(n-1)}{2}\right] + \frac{x_1 n(2n-1)}{2K(n-1)}\left[\frac{n_{12}}{(x_1+x_2n_{12})^2} - \frac{n_{21}}{(x_2+x_1n_{21})^2}\right] \tag{5}$$

Gothard's relation satisfies the Gibbs–Duhem equation and the necessary condition that G^E be zero at $x=0$ and $x=1$. At infinite dilution we have

$$n^{\infty} = 2 \tag{6}$$

For systems showing negative deviations from Raoult's law both n_{12} and n_{21} will be smaller than unity and in the intermediate range $0<x<1$ we have that the number of interacting neighbor molecules is

$$1 < n < 2 \tag{7}$$

For all other cases n will be larger than 2.

The activity coefficients at infinite dilution are

$$\ln \gamma_1^{\infty} = \frac{3}{K}\left(n_{21} - \frac{1}{n_{12}}\right) \tag{8}$$

$$\ln \gamma_2^{\infty} = \frac{3}{K}\left(n_{12} - \frac{1}{n_{21}}\right) \tag{9}$$

so that

$$\frac{\ln(\gamma_1^{\infty})}{\ln(\gamma_2^{\infty})} = \frac{n_{21}}{n_{12}} \tag{10}$$

Since G^E must have at least one extreme value, we have

$$\frac{dG^E/RT}{dx_1} = \ln\left(\frac{\gamma_1}{\gamma_2}\right) = 0 \tag{11}$$

and from Eqns. 4, 5 and 11,

$$\frac{n(2n-1)}{2K(n-1)}\left[\frac{n_{12}}{(x_1^*+x_2^*n_{12})^2} - \frac{n_{21}}{(x_2^*+x_1^*n_{21})^2}\right] = 0 \tag{12}$$

where $x_1 = x_1^*$ is the concentration at the extreme value of G^E.

Since $n > 1$ we must have, from Eqn. 12

$$\frac{n_{12}}{n_{21}} = \left[\frac{x_1^* + x_2^* n_{12}}{x_2^* + x_1^* n_{21}}\right]^2 \tag{13}$$

Equation 13 is a quadratic in n_{12} (or n_{21}) that can be solved to give two roots which relate n_{12} with n_{21}:

$$n_{12} = \frac{1}{n_{21}} \tag{14}$$

$$\frac{n_{12}}{n_{21}} = \left(\frac{x_1^*}{x_2^*}\right)^2 \tag{15}$$

However, Eqn. 14 is physically unacceptable.

An very interesting consequence of Eqn. 15 is that the ratio of the activity coefficients at infinite dilution is related to the composition at the extreme value of G^E. In effect, comparing Eqns. 10 and 15 we have

$$\frac{\ln \gamma_1^\infty}{\ln \gamma_2^\infty} = \frac{n_{21}}{n_{12}} = \left(\frac{x_2^*}{x_1^*}\right)^2 \tag{16}$$

Equation 13 can also be solved to give the composition at the extreme of n in terms of the two adjustable parameters n_{12} and n_{21}:

$$x_1^* = \frac{\sqrt{n_{12}}(1 - \sqrt{n_{12} n_{21}})}{\sqrt{n_{12}}(1 - n_{12}) + \sqrt{n_{21}}(1 - n_{21})} \tag{17}$$

with $0 < x_1^* < 1$. It should be noted that both G^E/RT and n reach their extreme values at $x_1 = x_1^*$.

The fact that $g = G^E/RT$ has an extreme value can be used to separate the parameters in other two-parameter equations like Margules and Van Laar (see appendix).

The capability of the Gothard model for predicting phase separation (liquid-liquid) can be explored applying one of the following two criteria (Walas, 1985):

$$\left(\frac{\partial^2 G^E}{\partial x_1^2}\right)_{P,T} + \frac{RT}{x_1 x_2} \leqslant 0 \tag{18}$$

or

$$\left[\frac{\partial \ln(\gamma_1)}{\partial x_1}\right]_{P,T} + \frac{1}{x_1} < 0 \tag{19}$$

Using Eqns. 1 and 18 we get, after simplification

$$\frac{2n-1}{n(n-1)}\frac{d^2n}{dx_1^2}-\frac{2n^2-2n+1}{n^2(n-1)^2}\left(\frac{dn}{dx_1}\right)^2+\frac{\mathrm{K}}{x_1x_2}\leqslant 0 \tag{20}$$

with

$$\frac{dn}{dx_1}=-\frac{n^2}{2}\left[\frac{n_{12}}{(x_1+n_{12}x_2)^2}-\frac{n_{21}}{(x_2+n_{21}x_1)^2}\right] \tag{21}$$

$$\frac{d^2n}{dx_1^2}=-n\left[\frac{n_{12}}{(x_1+n_{12}x_2)^2}-\frac{n_{21}}{(x_2+n_{21}x_1)^2}\right]\frac{dn}{dx_1}$$

$$+n^2\left[\frac{n_{12}(n_{12}-1)}{(x_1+n_{12}x_2)^3}-\frac{n_{21}(n_{21}-1)}{(x_2+n_{21}x_1)^3}\right] \tag{22}$$

There is no simple way of determining the conditions that the adjustable parameters n_{12}, n_{21} and K must comply in order that Eqn. 20 be satisfied. Nevertheless, if we assume that the criteria given by it should be satisfied for $x=0.5$ Eqn. 20 becomes

$$\mathrm{K}\geqslant -\frac{1}{4}\left[\frac{2n-1}{n(n-1)}\frac{d^2n}{dx_1^2}-\frac{2n^2-2n+1}{n^2(n-1)^2}\left(\frac{dn}{dx_1}\right)^2\right] \tag{23}$$

If within the framework of lattice theories we wish to attribute a physical meaning to the parameters of the Gothard model, then the K parameter can be identified with the order parameter s and we will have $\mathrm{K}=4s$ (Moelwyn–Hughes, 1961). This limits the range of K from zero (total disorder) to four (complete order). However, since Gothard treated K as a rather empirical third parameter, we can extend its range to any negative or positive value. On this basis we have proceeded to plot the contours of Eqn. 23 for different values of K (Figure 1).

Calculation of the adjustable parameters

In addition to the optimization procedure employed by Gothard (1985) for obtaining the values of n_{12} and n_{21}, we can use the following alternative methods, suggested by the model equations.

a) A plot of G^E/RT will give the values of the extreme coordinates which can be used to solve Equations 3 and 13 together and separate n_{12} from n_{21}.

From Eqns. 3 and 15 we get

$$n_{12}=(n^*-1)\frac{x_1^*}{x_2^*} \tag{24}$$

$$n_{21}=(n^*-1)\frac{x_2^*}{x_1^*} \tag{25}$$

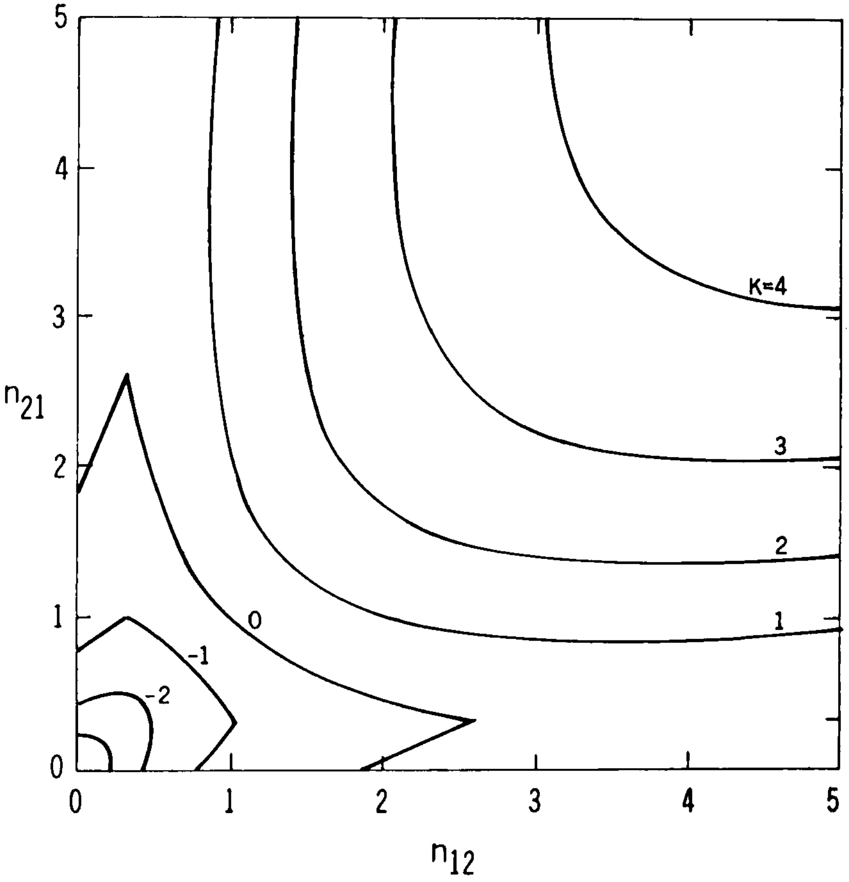

Figure 1 Incipient phase separation for $x = 0.5$.

where n^* is the value of n at the extremum of G^E. In other words, utilization of the extreme value of G^E/RT allows a simple separation of the parameters n_{12} and n_{21}.

b) The values of G^E/RT can be used to plot n as a function of composition x_1. Equation 1 may be written

$$\delta(x_1) = 2\exp\left[\frac{4G^E(x_1)}{RT}\right] \tag{26}$$

where $\delta(x)$ is an auxiliary function so that

$$n(x_1) = \frac{1+\sqrt{1+4\delta(x_1)}}{2} \tag{27}$$

For $x_1 = 0.5$ Eqn. 3 yields

$$\left(\frac{2}{n}\right)_{x=0.5} = \frac{1}{1+n_{12}} + \frac{1}{1+n_{21}} = A = \frac{4}{1+\sqrt{1+4\delta(1/2)}} \tag{28}$$

so that

$${}^{1}{}_{2} = \frac{2 - A + (1 - A)n_{21}}{(A - 1) + A n_{21}} \tag{29}$$

Equation 29 is then substituted in Eqn. 13 to obtain the value of n_{21}.

c) The values of $n(x_1)$ can be read at $x_1 = 0.5$ and say, $x_1 = 0.25$,

$$\left(\frac{2}{n}\right)_{x_1 = 0.25} = \frac{1}{1 + 3n_{12}} + \frac{3}{3 + n_{21}} = B \tag{30}$$

Combining together Eqns. 29 and 30 we get

$$B = \frac{(A - 1) + A n_{21}}{(5 - 2A) + (3 - 2A)n_{21}} + \frac{3}{3 + n_{21}} \tag{31}$$

Equation 31 is a quadratic in n_{21} with roots

$$n_{21} = \frac{(A + 7B - 4AB - 4) \pm 2\sqrt{(A - 1)(B - 1)(4 - A - B + AB)}}{A - 3B + 2AB} \tag{32}$$

and using Eqn. 29

$$n_{12} = \frac{(7A + B - 4AB - 4) \pm 2\sqrt{(A - 1)(B - 1)(4 - A - B + AB)}}{3(-3A + B + 2AB)} \tag{33}$$

d) If the system has an azeotropic point we can use this information as follows: At the azeotropic point we have

$$\left[\left(\frac{\partial g}{\partial x_1}\right)_{P,T} = \ln\left(\frac{\gamma_1}{\gamma_2}\right) = \ln\left(\frac{P_2^0}{P_1^0}\right)\right]^{\mathrm{Az}} \tag{34}$$

Using Eqn. 34 together with the definition of g yields

$$\left\{\frac{n(2n - 1)}{2\mathrm{K}(n - 1)}\left[\frac{n_{21}}{(x_2 + n_{12}x_1)^2} - \frac{n_{12}}{(x_1 + n_{21}x_2)^2}\right] = \ln\left(\frac{P_2^0}{P_1^0}\right)\right\}^{\mathrm{Az}} \tag{35}$$

Also

$$\left\{g = \frac{1}{\mathrm{K}} \ln \frac{n(n - 1)}{2} = \ln P - (x_1 \ln P_1^0 + x_2 \ln P_2^0)\right\}^{\mathrm{Az}} \tag{36}$$

Simultaneous solution of Eqns. 35 and 36 will yield the pertinent values of n_{12} and n_{21}. It should be clear that the accuracy of this method depends on the accuracy of the azeotropic data.

Glossary

A, B	Constants in the Margules and Van Laar equations
a, b	Constants in the Hajra equation
δ	Auxiliary function defined by Eqn. 26
G^E	Excess Gibbs function
g	Dimensionless parameter equal to G^E/RT
K	Parameter of the model, Eqn. 2
n	Parameter defined by Eqn. 2
n_{ij}	Parameters of the model
R	Universal gas constant
T	Absolute temperature
x_i	Liquid phase composition of component i
γ_i	Activity coefficient of component i

Indexes

Az	Azeotrope
i	Component i
$*$	Value of property at extreme value of g
∞	Infinite dilution

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APPENDIX

The fact that $g = G^E/RT$ must have at least one extreme value (g^*) can be used to separate the constants in the two-parameter Margules, Van Laar and Hajra (1980) models as follows:

a) Margules equation (Walas, 1985)

For the Margules model we have

$$g = Ax_1x_2^2 + Bx_1^2x_2 \tag{40}$$

$$\ln \gamma_1 = x_2^2[A + 2(B - A)x_1] \tag{41}$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B)x_2] \tag{42}$$

so that

$$A=-\left[g\frac{3x_1-2}{x_1x_2^2}\right]^* \tag{43}$$

$$B=\left[g\frac{3x_1-1}{x_1^2x_2}\right]^* \tag{44}$$

b) Van Laar equation (Walas, 1985)

In this case we have

$$g=\frac{ABx_1x_2}{Ax_1+Bx_2} \tag{45}$$

$$\ln\gamma_1=A\left[\frac{Bx_2}{Ax_1+Bx_2}\right]^2 \tag{46}$$

$$\ln\gamma_2=B\left[\frac{Ax_1}{Ax_1+Bx_2}\right]^2 \tag{47}$$

so that

$$A=\left[\frac{g}{x_1^2}\right]^* \tag{48}$$

$$B=\left[\frac{g}{x_2^2}\right]^* \tag{49}$$

c) Hajra equation

$$g=a_0x_1x_2e^{bx_1} \tag{50}$$

$$\ln\gamma_1=\frac{a_0x_2^2(1+bx_1)e^{bx_1}}{RT} \tag{51}$$

$$\ln\gamma_2=\frac{a_0x_1^2(1-b+bx_1)e^{bx_1}}{RT} \tag{52}$$

so that

$$a=\left[g\frac{e^{(x_1-x_2)x_2}}{x_1x_2}\right]^* \tag{53}$$

$$b=\left[\frac{x_1-x_2}{x_1x_2}\right]^* \tag{54}$$