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SOME PROPERTIES OF THE WOHL EQUATION FOR PHASE EQUILIBRIA

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The capability of the Wohl model for describing liquid-liquid equilibrium is discussed and criteria for incipient phase instability are determined. A new method is proposed for calculating the activity coefficients at infinite dilution.

KEY WORDS: Virial, activity coefficients

1 INTRODUCTION

In 1948 Wohl [1] proposed the following equation for describing the excess Gibbs energy of a multicomponent liquid mixture.

$$g = \frac{G^E}{RT} \sum (q_i x_i) \left[\sum z_i z_j a_{ij} + \sum z_i z_j z_k a_{ijk} + \dots \right] \quad (1)$$

In this equation q_i represent the effective volume of molecule i and z_i is the contribution of the same to the mole average of the effective volumes

$$z_i = \frac{q_i x_i}{\sum q_i x_i} \quad (2)$$

with $\sum z_i = 1$.

The terms a_{ij} , a_{ijk} , ... represent the energy of attraction in clusters formed by two, three, ... molecules so that the Wohl model may be considered the virial equation for the excess energy of a solution. This means that when considering the composition of any particular cluster at least one of the molecules must be different from the rest.

For a binary solution the three-suffix equation becomes

$$g = A x_1 z_2^2 + B x_2 z_1^2 \quad (3)$$

where

$$A = q_1(2a_{12} + 3a_{122}) \quad (4)$$

$$B = q_2(2a_{12} + 3a_{112}) \quad (5)$$

The activity coefficients of the Wohl model are given by

$$\ln \gamma_1 = z_1^2 \left[A + 2z_1 \left(B \frac{q_1}{q_2} - A \right) \right] \quad (6)$$

$$\ln \gamma_2 = z_2^2 \left[B + 2z_2 \left(A \frac{q_2}{q_1} - B \right) \right] \quad (7)$$

From Eqs. (6) and (7) it is seen that the Wohl model has three adjustable parameters, A , B , and $Q = q_1/q_2$. In principle, parameters A and B can be determined from the value of the activity coefficients at infinite dilution

$$\ln \gamma_1^\infty = A \quad (8)$$

$$\ln \gamma_2^\infty = B \quad (9)$$

By assuming particular expressions for the third parameter Q , Eqs. (6) and (7) reduce to other well known expressions for G^E . For example, if $q_1/q_2 = 1$ we obtain the Margules model and if $q_1/q_2 = A/B$ we get the Van Laar model. Calculation of the parameters in Eqs. (6) and (7) is not easy because two of them appear as their product. Wisniak and Apelblat [2] have developed graphical and numerical methods for determining the values of the parameters and provided numerical values for about 70 binary systems. An interesting consequence of their results is that only 31% of the systems studied were "pure" Wohl systems, of the rest 59% corresponded to the especial case $q_1/q_2 = A/B$ and for the other 10% $q_1/q_2 = 1$.

An additional method for calculating the Wohl parameters is to take advantage of the fact that the curves of $G^E(x)$ always have an extreme internal value at $x = x^*$ and that at that particular concentration $\gamma_1 = \gamma_2$. In other words, in addition to Eq. (3) we have

$$\frac{dg}{dx_1} = \frac{A + (2BQ^2 - 3A - AQ)x_1 + 3(A - BQ^2)x_1^2 + (Q - 1)(A - BQ^2)x_1^3}{(x_2 + Qx_1^3)} \quad (10)$$

Solving Eqs. (3) and (10) yields

$$\frac{A}{RT} = g_{\max} + \frac{2g_{\max}x_2^*}{x_1^*} - \frac{g_{\max}(x_1^*)^2 Q^2}{(x_2^*)^2} + 2g_{\max} Q \quad (11)$$

$$\frac{B}{RT} = g_{\max} + \frac{2g_{\max}x_1^*}{x_2^*} - \frac{g_{\max}(x_2^*)^2}{(x_1^*)^2 Q^2} + \frac{2g_{\max}}{Q} \quad (12)$$

A comparison of Eqs. (8),(9) with Eqs. (11),(12) indicates that the activity coefficients at infinite dilution may be calculated using the coordinates of the extreme value of G^E , located in a concentration range of very good analytical accuracy.

We will now explore the possibility for the Wohl equation to predict phase separation in a binary system. In order for a binary system to be stable the following condition must be satisfied at constant P and T [3]:

$$\frac{\partial^2 G^E/RT}{\partial x_1^2} + \frac{1}{x_1 x_2} \leq 0 \tag{13}$$

In addition, the following two additional relations must be satisfied at the incipient critical temperature of solution:

$$\frac{\partial^3 G^E/RT_c}{\partial x_1^3} + \frac{x_1 - x_2}{x_1^2 x_2^2} = 0 \tag{14}$$

$$\frac{\partial^4 G^E/RT_c}{\partial x_1^4} + 2 \frac{1 - 3x_1 x_2}{x_1^3 x_2^3} > 0 \tag{15}$$

Applying Eqs. (13) and (14) to the Wohl expression (Eq. (3)) we get

$$\frac{\partial^2 g}{\partial x_1^2} = \frac{2Q(BQx_2 - 2Ax_2 + AQx_1 - 2BQ^2x_1)}{(x_2 + Qx_1)^4} \tag{16}$$

$$\frac{\partial^3 g}{\partial x_1^3} = \frac{6Q[Q\{3A + B - 2BQ - x_1(A + B + Q(A + B - 2BQ))\} - 2Ax_2]}{(x_2 + Qx_1)^5} \tag{17}$$

$$\frac{\partial^4 g}{\partial x_1^4} = \frac{24(Q - 1)Q[2Ax_2 + Q\{-4A - B + 3BQ + x_1(A + B)(1 + Q) - 2BQ^2x_1\}]}{(x_2 + Qx_1)^6} \tag{18}$$

Replacing Eqs. (16) and (17) in Eqs.(13) and (14) respectively and solving for zero we get finally

$$\frac{A}{RT_c} = \frac{(x_2 + Qx_1)^3(7Qx_1 + x_1^2 - 6Qx_1^2 - 4Q^2x_1^2 - x_1^3 - Qx_1^3 + 2Q^2x_1^3 - x_2)}{6Q^2x_1^2x_2^2} \tag{19}$$

$$\frac{B}{RT_c} = \frac{(x_2 + Qx_1)^3(8Qx_1 + 2x_1^2 - 9Qx_1^2 - 2Q^2x_1^2 - 2x_1^3 + Qx_1^3 + Q^2x_1^3 - 2x_2)}{6Q^3x_1^2x_2^2} \tag{20}$$

Equations (19) and (20) have been solved in the range $0.01 \leq x_1 \leq 1.0$ for values of Q between 0.25 and 4, subject to the condition given by Eq.(15). The results are plotted

in Figure 1 for different values of Q , in particular $Q = 1$ and $Q = A/B$. The valid range of compositions for each value of Q is given in Table 1.

The results given in Table 1 indicate that mutual solubility increases as the value of Q increases.

It should be noted that the curves shown in Figure 1 must necessarily be symmetric around the axis $A = B$. Figure 1 also includes lines of constant critical composition $x^{a\beta}$ which show the interesting characteristic of having a maximum value that lies on the geometric locus of Van Laar, that is on $Q = A/B$.

Table 1 Composition range for different values of Q

Q	$X_{1,\min}$	$X_{1,\max}$
0.25	0.6669	0.9318
0.50	0.4587	0.8652
1.00	0.2619	0.7381
2.00	0.1384	0.5413
4.00	0.0682	0.3331
A/B	0.0100	0.9900

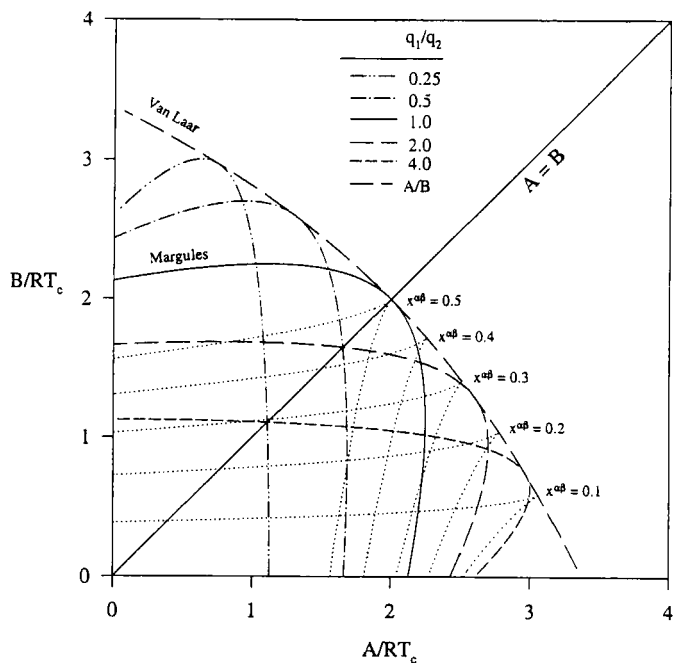


Figure 1

Eqs. (6) and (7) may also be used to calculate curves of isoactivity where

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta \tag{21}$$

$$x_2^\alpha \gamma_2^\alpha = x_2^\beta \gamma_2^\beta \tag{22}$$

where α and β represent the two liquid phases in equilibrium. Equations (21) and (22) can be solved simultaneously for a given value of Q , and the pertinent results are shown in Figures 2 and 3 for $Q=0.25$ and $Q=0.50$. As a practical example of the use of these curves, consider the case for which $(A/RT_c)_{Q=0.25} = 3.10$ and $(B/RT_c)_{Q=0.25} = 3.15$. From Figure 2 we obtain $x_1^\alpha = 0.05$ and $x_2^\beta = 0.98$ as the composition of the two liquid phases in equilibrium. Due to symmetry characteristics of the Wohl model the pertinent intersection will also represent the compositions $x_1^\alpha = 0.02$ and $x_2^\beta = 0.95$ for the case where $(A/RT_c)_{Q=4} = 3.10$ and $(B/RT_c)_{Q=4} = 3.15$.

From Figures 2 and 3 we infer that systems which are highly immiscible will correspond to small values of Q (or large values of its reciprocal). There are only two Eqs. (21 and 22) available to determine the three adjustable parameters, hence we

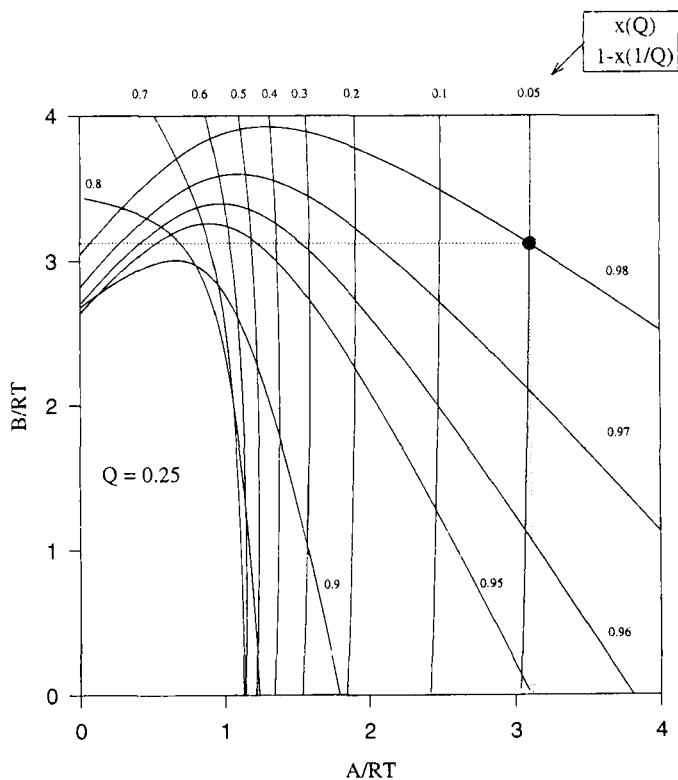


Figure 2

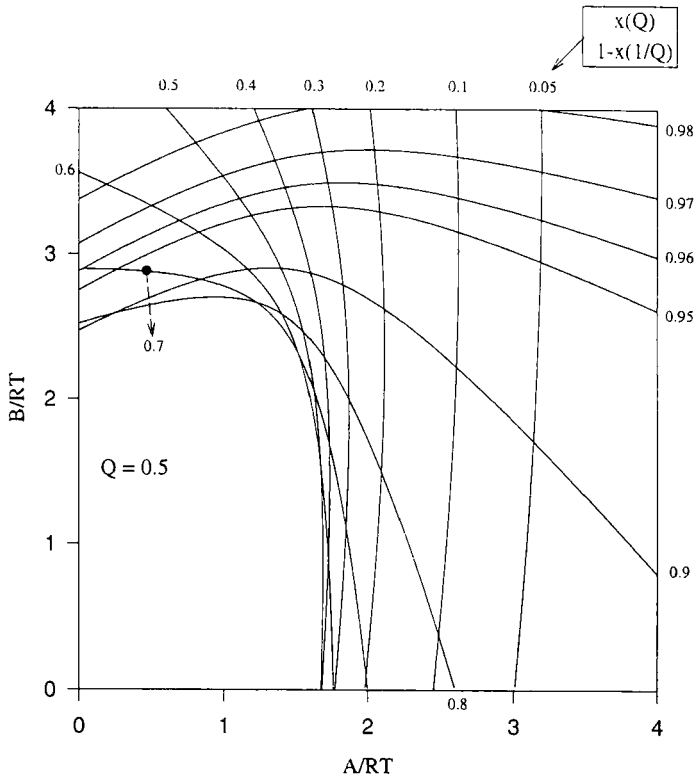


Figure 3

can look at Q as a highly flexible parameter that allows representation of many immiscible systems.

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