

# Calculation of the activity coefficients and vapour composition from equations of the Tao method modified for inconstant integration step $\Delta x$ . II. Ternary systems

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A simple method for calculating the activity coefficients of components in liquid phase and vapour composition of ternary systems is presented. The calculation is based on the data of vapour pressure of liquid solutions of known composition measured along the lines of constant ratio of the molar fractions of both components. The equations of the Tao method modified for inconstant integration step  $\Delta x$  are applied. By means of the equations thus modified it is possible to calculate the equilibrium data immediately for individual experimental points.

The equations of the *Tao* method [1] modified for the inconstant integration step [2] are suitable for the calculation of activity coefficients of the components of liquid solutions and vapour composition of binary systems from the experimental values of the total vapour pressure of liquid solutions of known composition. The aim of this study is to extend the applicability of these equations to the calculation of equilibrium data of ternary systems.

## *Equations of the modified Tao method for inconstant increment $\Delta x$ (Binary systems)*

The calculation of the ratio of activity coefficients of components from the  $P-x$  or  $t-x$  data found experimentally is based on the following fundamental equation of the method [2]

$$\left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,n}} = \frac{\left(\frac{\gamma_1}{\gamma_2}\right)^{\frac{x_{1,n} + x_{1,(n-1)}}{2}} - B_n C_n}{A_n C_n} \quad (1)$$

where

$$A_n = \frac{x_{1,n} P_1^0}{\Phi_1 P}, \quad (2)$$

$$B_n = \frac{(1 - x_{1,n}) P_2^0}{\Phi_2 P}, \quad (3)$$

$$C_n = \left[ \exp \left( \frac{x_{1,n} - x_{1,(n-1)}}{2} \Gamma_{x_{1,n}} \right) \right] \cdot \prod_{k=0}^{n-1} \left[ \left( \frac{\gamma_1}{\gamma_2} \right)^{\frac{x_{1,(k+1)} - x_{1,(k)}}{2}} \right]_{x_{1,k}}$$

$$\cdot \exp \left( \frac{x_{1,(k+1)} - x_{1,(k-1)}}{2} \Gamma_{x_{1,k}} \right) \Big] = C_{n-1} \left\{ \left( \frac{\gamma_1}{\gamma_2} \right)_{x_{1,(n-1)}}^{\frac{x_{1,n} - x_{1,(n-2)}}{2}} \cdot \exp \left[ \frac{x_{1,n} - x_{1,(n-1)}}{2} (\Gamma_{x_{1,n}} + \Gamma_{x_{1,(n-1)}}) \right] \right\} \quad (4)$$

If the subscript  $(k-1) = 0$  or  $-1$ , then the zero value must be inserted for  $x_{1,(k-1)}$  in eqn (4). Provided we limit ourselves only to isothermal equilibrium conditions, the term  $\Gamma = \frac{\Delta \mathbf{V}}{RT^2} \left( \frac{\partial P}{\partial x_1} \right)_T$  frequently assumes a very small value [3].

In this case, the effect of  $\Gamma$  on the calculation may be neglected.

Iteration method is suitable for solving eqn (1), the value of  $(\gamma_1/\gamma_2)_{x_{1,(n-1)}}$  calculated for the preceding increment  $\Delta x_1$  being used as a starting value of  $(\gamma_1/\gamma_2)_{x_{1,n}}$ . The limiting activity coefficient  $\gamma_{1,0}$  necessary for the calculation of  $C_1$  according to eqn (4) may be determined for lower pressures from the relationship put forward by *Gautreaux and Coates* [4]

$$\lim_{x_1 \rightarrow 0} \gamma_1 = \gamma_{1,0} = \frac{P_2^0}{P_1^0} \left[ 1 + \left( \frac{\partial P}{\partial x_1} \right)_T \frac{1}{P_2^0} \right]. \quad (5)$$

If using eqn (1), we must care for the integration to be performed in the sense of increasing values of the total pressure and for the correct denotation of indices as pointed out in our preceding paper [2].

The individual activity coefficients  $\gamma_1$  and  $\gamma_2$  are fixed by the calculated value of  $\gamma_1/\gamma_2$  and the subsequent eqn

$$\frac{P_1^0 x_1}{P \Phi_1} \left( \frac{\gamma_1}{\gamma_2} \right) + \frac{P_2^0 x_2}{P \Phi_2} = \frac{1}{\gamma_2} \quad (6)$$

The composition of the vapour phase can be calculated from the equilibrium condition

$$P y_i \Phi_i = P_i^0 x_i \gamma_i, \quad (7)$$

where for a low pressure in the system the correction coefficient  $\Phi_i$  may be considered to depend only on the properties of pure components at a given pressure and temperature. The approximate calculation of this coefficient can be performed by means of the following equation

$$\ln \Phi_i = \frac{(P_i^0 - P) (\mathbf{V}_i^L - B_{ii})}{RT} \quad (8)$$

### Calculation of $\gamma_i$ and $y_i$ of ternary systems

In order to apply the above-mentioned working equations also to ternary systems, we assumed equal limitation as *Chang and Lu* [5] who used the coexistence equation for the calculation. In this approach the ternary solutions are regarded as quasi-binary systems while one component — the hypothetical — of such system is represented by the binary solution with a constant weight ratio of the components. The variations in the composition of these quasi-binary systems with a constant ratio of the mole fractions of both components may be illustrated on a triangular diagram (Fig. 1).

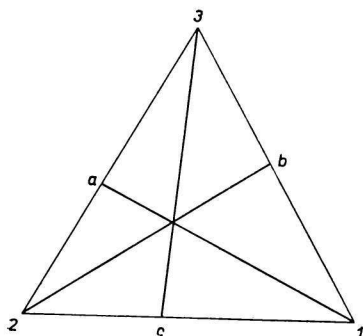


Fig. 1.

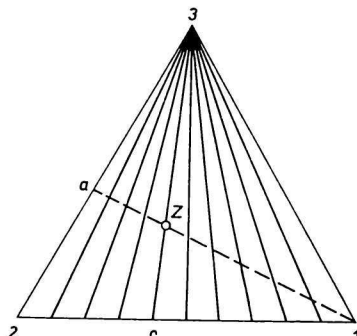


Fig. 2.

For instance, the solutions one component of which is represented by component 3 and the second component by hypothetical pure component  $c$  consisting of a binary mixture of components 1 and 2 (point  $c$ ) correspond to the connecting line  $\overline{3c}$ . It may be written for each point of this line

$$c = (x_2)_{\text{binary } 1-2} = \left( \frac{x_2}{x_1 + x_2} \right)_{\text{ternary}} = \text{const.}$$

The parameter  $c$  can assume the values from 0 to 1 and is used for denoting the individual lines  $\overline{3c}$ .

In a similar way it is possible to create quasi-binary systems with a constant weight ratio of components 2 and 3 (line  $\overline{1a}$ ) or 1 and 3 (line  $\overline{2b}$ ).

### Calculation of $\gamma_3$ and $y_3$

Let us assume that there are the experimental  $P-x$  data available for quasi-binary systems  $3-c$ , i.e. the data on vapour pressure of the solutions the composition of which is fixed by a series of straight lines  $\overline{3c}$  (Fig. 2). By using the modified equations of the Tao method the activity coefficients  $\gamma_3$  and mole fractions  $y_3$  can be calculated. If no azeotropic mixture exists, the component  $c$  of such solutions is always more volatile. Therefore all equations are formally so arranged before calculation that index 1 is replaced by index  $c$  and index 2 by index 3.

If the  $P-x_c$  relationship does not show any extremes, the calculation starts from point 3 ( $x_c = 0$ ). The starting value of the limiting activity coefficient of the hypothetical component  $c$  ( $\gamma_{c,0}$ ) is determined by means of eqn (5).

The saturated vapour pressure of hypothetical pure component  $c$  ( $P_c^0$ ) is given by the vapour pressure of the binary solution of components 1 and 2 the composition of which corresponds to point  $c$ .

The second virial coefficient of "component"  $c$  ( $B_{cc}$ ) may be calculated from the following equation

$$B_{cc} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}. \quad (9)$$

Provided the volume contraction accompanying mixing is negligible, it holds for the molar volume of "component"  $c$

$$\mathbf{V}_c^L = x_1 \mathbf{V}_1^L + x_2 \mathbf{V}_2^L. \quad (10)$$

In eqn (9),  $y_1$  and  $y_2$  are the mole fractions of the vapour phase which is in equilibrium with liquid solution  $c$ . These fractions may be calculated by means of eqns (1–7) for binary solution 1–2. The coefficient  $B_{12}$  is approximately determined as a geometrical mean of the  $B_{11}$  and  $B_{22}$  values.

### Calculation of $\gamma_1$ and $y_1$

The calculation requires that the set of the experimental  $P$ – $x$  data along each line  $\overline{3c}$  should be covered by a convenient function, e.g.

$$P = P_1^0 x_1 + P_2^0 x_2 + x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j. \quad (11)$$

Fig. 2 helps to clear up the method of the calculation of  $\gamma_1$  and  $y_1$ . It is possible to draw the corresponding straight line  $\overline{1a}$  going through an arbitrary experimental point  $Z$ . By determining the vapour pressure and composition of the liquid in the points of intersection of the straight line  $\overline{1a}$  with straight lines  $\overline{3c}$  we obtain a series of the  $P$ – $x$  values of the quasi-binary system 1– $a$  the hypothetical component  $a$  of which is represented by the binary solution of components 2 and 3 (point  $a$ ). The ratio of the mole fractions of components 2 and 3 in this solution is constant along the whole straight line  $\overline{1a}$ .

The calculation of  $\gamma_1$  and  $y_1$  in the experimental point  $Z$  may be summed up in the following steps.

1. The mole fraction of component 1 is fixed by the value of  $x_3$  in the experimental point  $Z$  on the straight line  $\overline{3c}$  as well as the value of parameter  $c$

$$x_1 = (1 - c)(1 - x_3). \quad (12)$$

By means of  $c$ ,  $x_1$ , and  $x_3$  it is possible to express both the equation of the straight line  $\overline{1a}$  going through a given point  $Z$  and the value of parameter  $a$

$$a = (x_2)_{\text{binary } 2-3} = \left( \frac{x_2}{x_2 + x_3} \right)_{\text{ternary}} = \text{const.}$$

The properties of hypothetical pure component  $a$ , i.e.  $P_a^0$ ,  $B_{aa}$ , and  $\mathbf{V}_a^L$  are calculated in a similar way as demonstrated for hypothetical component  $c$ .

2. By solving equation of the straight line  $\overline{1a}$  and equation of the first straight line  $\overline{3c}$  (the nearest to the  $\overline{23}$  side of triangle) the coordinates  $x_1$  and  $x_3$  of the point of intersection of these straight lines are determined. By means of the value of  $x_3$  thus determined and the known function  $P = f(x)$  for the first line  $\overline{3c}$  the value of vapour pressure  $P$  may be calculated.

3. The value of the limiting activity coefficient of component 1 ( $\gamma_{1,0}$ ) is determined. (We assume that the total pressure along the straight line  $\overline{1a}$  increases from point  $a$  to point 1.) The derivative  $\partial P / \partial x_1$  in eqn (5) will be approximated by the ratio of the differences  $\Delta P / \Delta x_1$  while the values of  $P$  and  $x_1$  occurring in the differences  $\Delta P = P_a^0 - P$  and  $\Delta x_1 = x_1$  have been determined in step 2.

4. The value of  $\gamma_1 / \gamma_a$  can be calculated from the basic eqn (1) and the values of  $\gamma_1$  and  $y_1$  can be obtained by means of eqns (6) and (7).

5. The second step is repeated for the point of intersection with the second line  $\overline{3c}$  and thus the values of  $P$  and  $x_1$  at the end of the second increment  $\Delta x_1$  along a given line  $\overline{1a}$  may be determined. The second step is followed by step 4. The start-

ing value for the solution of eqn (1) is given by the value of  $\gamma_1/\gamma_a$  calculated for the preceding point of intersection.

The calculation described in item 5 continues until the experimental point  $Z$  is reached.

#### Calculation of $\gamma_2$ and $y_2$

From the theoretical point of view there is nothing in the way of performing the calculation for component 2 on a similar principle. But we do not recommend the solution along the lines  $\overline{2b}$  for the following reasons. As obvious from Fig. 3, the first integration step  $\Delta x$  (given by the mole fraction of hypothetical component  $b$ ,  $x_b = 1 - x_2$ , in the point of intersection of straight line  $\overline{2b}$  with the first straight line  $\overline{3c}$ ) may attain an inadequately high value. That concerns mainly those points  $Z$  which occur in the upper part of the triangle. In such cases it is hardly possible to use the approximation  $\partial P/\partial x_b \doteq \Delta P/\Delta x_b$  for the calculation of the limiting activity coefficient of hypothetical component  $b$ .

For this reason it is more convenient to use the condition  $\sum y_i = 1$  or eqn (7) for the calculation of  $y_2$  and  $\gamma_2$ .

In connection with the calculation of the limiting activity coefficients and equilibrium composition of vapour phase by means of the modified equations of the Tao method, the selection of the basic set of the experimental  $P-x$  data is of importance. From a more detailed analysis of the three possible cases [6] it may be concluded that the selection of the solutions with the composition fixed by straight lines  $\overline{3c}$  will be most convenient for this purpose. Actually, only in this case it is possible to decide unambiguously which component of quasi-binary solutions along the straight lines  $\overline{3c}$  and  $\overline{1a}$  will be the more volatile or the less volatile. An advantage of this selection consists in the fact that the first increment for the integration along the straight line  $\overline{1a}$  is relatively small. These conditions need not be fulfilled if the experimental set of solutions is situated on line  $\overline{1a}$  or  $\overline{2b}$ .

The above-mentioned method for calculating the activity coefficients and composition of vapour phase was applied to the ternary system acetone—2-propanol—water at 75°C\*. The  $P-x$  data on three binary systems as well as the data on the quasi-binary solutions 3— $c$  (for  $c = 0.1, 0.2, 0.35, 0.5, 0.65, 0.8$ , and  $0.9$ ) have been taken from the paper by Drolet [7].

For the calculation of the values of  $\gamma_3$  and  $y_3$  along each line  $\overline{3c}$  it proved con-

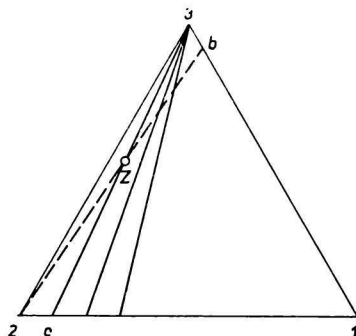


Fig. 3.

\* The results of calculation are given in [6].

venient to repeat several times the complete computation with a new starting value of the limiting activity coefficient of hypothetical component  $c$  obtained from the Redlich—Kister equation of fourth order. The coefficients of this equation ( $b$ ,  $c$ ,  $d$ ) were determined from the calculated values of  $\gamma_c/\gamma_3$  processed by the method of least squares.

It is equally convenient to repeat the calculation of  $\gamma_1$  and  $y_1$  along the straight lines  $\bar{1}a$  with the refined values of  $\gamma_{1,0}$ . The approximation  $\partial P/\partial x_1 \doteq \Delta P/\Delta x_1$  used for the determination of the first values of the limiting activity coefficients need not be satisfactory for each line  $\bar{1}a$ . Since the number of lines  $\bar{1}a$  is given by the number of ternary experimental points and therefore exceeds considerably the number of lines  $\bar{3}c$ , we preferred in this case to correlate the whole set of the calculated values of  $\gamma_1$  and  $\gamma_3$  with the Redlich—Kister equation for ternary solutions containing nine binary (calculated for individual binary systems) and three ternary coefficients. The ternary coefficients were calculated by the method of least squares.

Besides the limiting activity coefficients, the density of the experimental  $P-x$  data, the adequate number of lines  $\bar{3}c$  (as a rule, it satisfies if  $c$  is changed by 0.1) and the accuracy of the pressure interpolation will influence the accuracy of the calculation of  $\gamma_i$  and  $y_i$ .

### Symbols

- $a$  parameter identical with the mole fraction  $x_2$  of a binary solution of components 2 and 3 or giving a constant ratio of the mole fractions of components 2 and 3 in ternary liquid solutions
- $A$  coefficient occurring in the relationship between the vapour pressure and composition of solution
- $B_{ii}$  second virial coefficient of pure component  $i$
- $B_{12}$  interaction virial coefficient of components 1 and 2
- $c$  parameter identical with the mole fraction  $x_2$  in a binary solution of components 1 and 2 or giving a constant ratio of the mole fractions of components 1 and 2 in ternary liquid solutions
- $P_i^0$  saturated vapour pressure of pure component  $i$
- $P$  saturated vapour pressure over solution
- $R$  gas constant
- $T$  absolute temperature
- $V_i^L$  molar volume of pure liquid component  $i$
- $\Delta V$  molar mixing volume of solution
- $x_i$  mole fraction of the component  $i$  in liquid phase
- $y_i$  mole fraction of the component  $i$  in vapour phase
- $\gamma_i$  activity coefficient of the component  $i$  in liquid solution
- $\gamma_{i,0}$  limiting activity coefficient of the component  $i$  ( $\gamma_{i,0} = \lim_{x_i \rightarrow 0} \gamma_i$ )
- $\Gamma = \frac{\Delta V}{RT} \left( \frac{\partial P}{\partial x_i} \right)_T$  for isothermal equilibrium conditions
- $\Phi_i$  coefficient expressing the non-ideal behaviour of vapour phase and the effect of pressure on the properties of components in liquid

Subscripts 1, 2, and 3 denote the components of ternary system and  $a$ ,  $b$ ,  $c$  the hypothetical pure components of quasi-binary solutions.

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