Calculation of the activity coefficients and vapour composition from equations of the Tao method modified for inconstant integration step Δx. I. Binary systems

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Basic equations of the original Tao method for calculating the binary liquid—vapour equilibrium from $P-x$ or $t-x$ data were modified for the inconstant integration step Δx. The modified equations enable to calculate the activity coefficients of components and the vapour phase composition directly in the experimental points; the functional relationship of the $P-x$ or $t-x$ data need not be known. The modified form of the basic equation provides a convergence of the iterative solution. An inevitable condition of the solution is to carry out the calculation in the direction of the increasing values of the total pressure, analogously to the integration of the coexistence equation.

The *Tao* method [1] for calculating the activity coefficients of the components of the liquid solution and the vapour phase composition from the $P-x$ or $t-x$ data was derived from the condition of the equilibrium, from the material balance of one mole of the vapour phase, from the relationship defining the molar excess free enthalpy of the solution, and from its exact differential. Tao derived a basic equation of the method for computing the ratio of the activity coefficients of the liquid-phase components by integrating with a constant increment $\Delta x_1 = \varepsilon$ and applying the trapezoid rule for the solution of integral (the dependence of the integrand on x_1 is only slightly curved). The method is usually called rigorous as it is based only on exact thermodynamic relationships.

In comparison with other rigorous methods [2—4], the advantage of the Tao method is that it is not too sensitive to the size of the integration step ε. While in the Tao method it is sufficient to choose $\varepsilon = 0.05$ as a rule, in other methods ε is usually smaller, frequently as low as 0.001. It is then reflected in the preliminary processing of the experimental $P-x$ or $t-x$ data. In the methods sensitive to the size of ε, the experimental $P-x$ data are first processed in the form of a convenient function, *e.g.* a polynomial. The examination of the convenient form and degree of the polynomial of the $P-x$ dependence is often a substantial part of the whole calculation. The Tao method simplifies this procedure since the values of the total pressure in the individual points determined by the increment are read off from the graph of the experimental $P-x$ curve.

In this paper we present basic equations of the Tao method modified for the inconstant integration step Δx_1. Such modified equations make it possible to calculate

the activity coefficients of components and the composition of the vapour phase for the experimental $P-x$ or $t-x$ values, without any interpolation. With respect to the usual density of the experimentally determined equilibrium data, sufficiently precise results may be expected when the increments Δx are less than 0.1.

Theoretical

The derivation of basic equations for the inconstant integration step follows from the same considerations as described by *Tao* [1]. The equilibrium state defined by equal fugacities of components in both the liquid and the vapour phase of the binary system, can be expressed by relation

$$P_i^0 \, x_i \, \gamma_i = P \, y_i \, \Phi_i. \tag{1}$$

The material balance of vapour phase is

$$y_1 + y_2 = 1. \tag{2}$$

Combining eqns (1) and (2) yields the first of basic equations of the method

$$\frac{P_1^0 \, x_1}{P \, \Phi_1} \left(\frac{\gamma_1}{\gamma_2} \right) + \frac{P_2^0 \, x_2}{P \, \Phi_2} = \frac{1}{\gamma_2}. \tag{3}$$

The exact differential of the molar excess free enthalpy of the binary solution can be written as

$$d \left(\frac{\Delta G^{\mathrm{E}}}{RT} \right) = \frac{\Delta V}{RT} \, dP - \frac{\Delta H}{RT^2} \, dT + \ln \frac{\gamma_1}{\gamma_2} \, dx_1. \tag{4}$$

The molar excess free enthalpy is defined by equation

$$\frac{\Delta G^{\mathrm{E}}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2. \tag{5}$$

The expression for $\Delta G^{\mathrm{E}}/RT$ from eqn (5) is inserted into eqn (4), then multiplied by dx_1/dx_1 and integrated in the limits $x_{1,(n-1)}$, $x_{1,n}$, where the first subscript of x stands for the component and the second for the ordinal number of the experimental point. The integral is solved using the trapezoid rule and we get

$$\frac{x_{1,n} - x_{1,(n-1)}}{2} \ln \left(\frac{\gamma_1}{\gamma_2} \right)_{x_{1,n}} = \ln \left(\frac{1}{\gamma_2} \right)_{x_{1,n}} - \ln \left(\frac{1}{\gamma_2} \right)_{x_{1,(n-1)}} +$$

$$+ \frac{x_{1,n} + x_{1,(n-1)}}{2} \ln \left(\frac{\gamma_1}{\gamma_2} \right)_{x_{1,(n-1)}} + \frac{x_{1,n} - x_{1,(n-1)}}{2} (\Gamma_{x_{1,n}} + \Gamma_{x_{1,(n-1)}}), \tag{6}$$

where

$$\Gamma = - \frac{\Delta H}{RT^2} \left(\frac{\partial T}{\partial x_1} \right)_P \quad \text{for isobaric}$$

or

$$\Gamma = \frac{\Delta V}{RT^2} \left(\frac{\partial P}{\partial x_1} \right)_T \quad \text{for isothermic conditions}$$

of the equilibrium.

When eqn (6) is written for each successive integration step given by a pair of the consecutive experimental points, i.e. from $x_{1,0} = 0$ to $x_{1,1}$, from $x_{1,1}$ to $x_{1,2}$ etc., the summation of these equations and their rearrangement yields the second basic equation of the method

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

$$
\left. \prod_{k=0}^{n-1} \left[\left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,k}}^{\frac{x_{1,(k+1)} - x_{1,(k-1)}}{2}} \exp\left(\frac{x_{1,(k+1)} - x_{1,(k-1)}}{2} \Gamma_{x_{1,k}}\right) \right] \right\}. \tag{7}
$$

It is noteworthy that the zero value has to be inserted for the mole fraction $x_{1,(k-1)}$ if the subscript $(k-1) = 0$ or -1.

Combination of basic eqns (3) and (7) yields the main equation of the method with the ratio of the activity coefficients as the only unknown

$$
\left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,n}}^{\frac{x_{1,n} + x_{1,(n-1)}}{2}} = \left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,n}} A_n C_n + B_n C_n. \tag{8a}
$$

After a simple rearrangement

$$
\left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,n}} = \frac{\left(\frac{\gamma_1}{\gamma_2}\right)_{x_{1,n}}^{\frac{x_{1,n} + x_{1,(n-1)}}{2}} - B_n C_n}{A_n C_n}, \tag{8b}
$$

where

$$
A_n = \frac{x_{1,n} P_1^0}{\Phi_1 P}, \tag{9}
$$

$$
B_n = \frac{(1 - x_{1,n}) P_2^0}{\Phi_2 P}, \tag{10}
$$

and

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

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

$$
\left. \exp\left[\left(\frac{x_{1,n} - x_{1,(n-1)}}{2}\right) (\Gamma_{x_{1,n}} + \Gamma_{x_{1,(n-1)}}) \right] \right\}. \tag{11}
$$

For $k = 0$, the ratio $(\gamma_1/\gamma_2)_{x_{1,k}}$ in eqn (11) is equal to the limiting activity coefficient of the component 1, $\gamma_{1,0}$. Its value may be determined from the slope of the tangent line to the $P-x$ curve at $x_1 \to 0$ [10].

The calculation starts with the iterative solution of eqn (8), thus obtaining γ_1/γ_2 value. The individual values of the activity coefficients are calculated from eqn (3) and the vapour phase composition for the first experimental point from eqn (1). The $(\gamma_1/\gamma_2)_{x_{1,(n-1)}}$ value calculated in the previous experimental point $(n-1)$ is used as a starting value of $(\gamma_1/\gamma_2)_{x_{1,n}}$ for each solution. The detailed solution procedure including the block scheme is described in the Tao's work.

The basic equation in the form of (8a) is similar to that for the constant integration step ε (in the Tao's paper denoted as eqn (8)). The form (8b) obtained through a simple rearrangement is more advantageous for the γ_1/γ_2 evaluation since it provides a convergence of iterations even in cases where the form (8a) is not valid. The sufficient condition of the convergence of the solution of eqn (8) requires absolute value of the first derivative of the right side of equation with respect to γ_1/γ_2 to be smaller than one. It is eqn (8b) which is better satisfies this condition. As an example, we can mention calculations of the activity coefficients from the $P-x$ data for several systems of the type of hydrocarbon—polar solvent [7] and the pairs of polar solvents [8] where the forms of the dependences log $(\gamma_1/\gamma_2) = f(x_1)$ are mutually very different. (Some of them show permanently decreasing or increasing trend of γ_1/γ_2 values with increasing x_1, others exhibit a maximum or a minimum on the curves of these dependences.)

Conditions for solving eqn (8) are the same as those for the solution of the coexistence equation. They are thoroughly described by *Van Ness* [5] and also emphasized by *Erdös* [6]. Eqn (8) must be always solved in the direction of the increasing total pressure. When the system shows an azeotropic point represented by a maximum of the total pressure on the $P-x$ curve, the calculation is carried out in two directions, from the point $x_1 = 0$ and from the point $x_2 = 0$ towards the azeotropic point. For the calculation from the point $x_2 = 0$, all equations have to be formally adapted by a mutual exchange of the subscripts 1 and 2. These conditions hold also for equations of the Tao method derived for the constant integration step ε, however, the author did not mentioned them.*

Illustrative calculation

Equations derived for the inconstant integration step Δx were tested with the system chloroform—ethanol. For this purpose, we used the experimental $P-x$ values of this system at 35°C published by *Scatchard* [9]. (Two points were omitted from the set of the experimental data because of the varying values of the total pressure.) Values of $\Gamma = 0$ were taken into calculation. With regard to the low pressure in the system, the correction factors Φ_1, Φ_2 were considered to be dependent only on the properties of pure components at a given pressure and temperature. They were calculated from the secondary virial coefficients and from the molar volumes of pure components presented in the same paper [9]. The iterative calculation according to eqn (8b) proceeded from the boundary values $x_1 = 0$ and $x_2 = 0$ towards the maximum on the curve of the $P-x$ values. The values of $\gamma_{1,0} = 1.480$

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* Several examples of azeotropic systems with the maximum of the total pressure were included in calculations carried out from the point $x_1 = 0$ directly to $x_1 = 1$. It was seen that eqn (8) had a real root even at the end of the first or second increment Δx after passing the maximum but the results were little precise. Both systems used by Tao for testing his method had the maximum of the total pressure close to $x_1 = 1$.

Table 1

Experimental $P - x, y$ data [9] and γ_1, γ_2, and y_1 values calculated from the modified Tao method

System chloroform (1)—ethanol (2) at 35°C

n		P [torr]	γ_1	γ_2	y_1^{calc}	y_1^{exp}
0	0	102.78	1.480	1.000	0	0
1	0.0062	104.87	1.510	1.000	0.0259	0.0254
2	0.0241	111.31	1.573	0.999	0.0991	0.0991
3	0.0297	113.61	1.616	0.999	0.1229	0.1210
4	0.0542	123.54	1.681	0.997	0.2146	0.2154
5	0.0594	125.82	1.699	0.996	0.2335	0.2343
6	0.1109	148.26	1.773	0.992	0.3867	0.3885
7	0.1730	177.60	1.848	0.986	0.5262	0.5304
8	0.2361	205.68	1.848	0.986	0.6215	0.6207
9	0.2873	225.06	1.799	0.995	0.6738	0.6747
10	0.3014	229.24	1.772	1.001	0.6841	0.6870
11	0.3227	236.50	1.750	1.007	0.7012	0.7009
12	0.3845	253.39	1.655	1.038	0.7384	0.7370
13	0.3922	255.28	1.643	1.043	0.7424	0.7412
14	0.4384	267.65	1.592	1.067	0.7677	0.7646
15	0.4827	274.04	1.504	1.119	0.7806	0.7797
16	0.4846	274.46	1.502	1.121	0.7815	0.7812
17	0.6185	291.95	1.312	1.324	0.8202	0.8181
18	0.6783	296.93	1.236	1.477	0.8336	0.8327
19	0.7746	303.05	1.135	1.855	0.8565	0.8554
20	0.8265	305.39	1.090	2.183	0.8710	0.8698
21	0.8483	306.25	1.074	2.347	0.8790	0.8783
22	0.9315	306.05	1.021	3.538	0.9176	0.9161
23	0.9560	304.87	1.004	4.700	0.9294	0.9363
24	0.9586	304.17	1.005	4.584	0.9351	0.9385
25	0.9616	303.91	1.003	4.780	0.9372	0.9414
26	1	295.11	1.000	5.556	1	1

and $\gamma_{2,0} = 5.556$ determined by *Tao* [1] were used as starting values of the limiting activity coefficients.

Experimental P, x_1, y_1 values [9] and the corresponding calculated γ_1, γ_2, and y_1 are listed in Table 1.

Symbols

ΔG^E	molar excess free enthalpy of solution
ΔH	molar mixing enthalpy of solution
P_i^0	saturated vapour pressure of pure component i
P	total pressure
R	gas constant
T	absolute temperature
ΔV	molar mixing volume of solution
x_i	mole fraction of the i component in liquid phase
y_i	mole fraction of the i component in vapour phase
γ_i	activity coefficient of the i component in liquid phase

Γ defined by eqns following eqn (6)

Φ_i correction for the non-ideal behaviour of vapour phase

   Subscripts 1 and 2 denote the more volatile component and the less volatile component respectively, n stands for the ordinal number of the experimental point.

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