Thermodynamics of Solutions

Numerical Method for Calculating Excess Free Energy and Activity Coefficients From Total Pressure Measurements

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THE DETERMINATION of vapor liquid equilibria for binary systems by the total pressure method has been developed and discussed (*2, 4*), and the advantages of the method have been recognized. The important advantage of being able to eliminate the lengthy and usually less accurate analytical determination of the vapor composition is a powerful incentive for using the method. However, further improvements are necessary in the area of data treatment to eliminate the "cut and try" aspects of calculating the activity coefficients. This article presents a more direct numerical calculational method, which can be operated with a hand calculator or a programmed digital computer, in place of the previous trial and error procedure (*2*, p. 1772, para. 3).

Since from measurements of total pressure the excess pressure can be obtained,

$$P_{12}^E = \pi_{actual} - \pi_{ideal} \tag{1}$$

the problem reduces essentially to one of finding the excess free energy function from the excess pressure function, and since

$$F_{12}^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \tag{2a}$$

the activity coefficients can be obtained,

$$RT\ln\gamma_1 = F_{12}^E + x_2\left(\frac{\partial F_{12}^E}{\partial x_1}\right) \tag{2b}$$

$$RT\ln\gamma_2 = F_{12}^E - x_1\left(\frac{\partial F_{12}^E}{\partial x_1}\right) \tag{2c}$$

A recent article (*1*) described a calculational method for obtaining the partial pressures from total pressure data, which in effect also determines the activity coefficients; however, the method makes the unnecessary assumption that the vapor phase is a perfect gas.

BASIC EQUATIONS

The primary concern here is with a set of total pressure data (bubble point) for a binary system as a function of composition at constant temperature. Such data can be obtained by different experimental methods, equilibrium still, ebulliometer, etc. Using an ebulliometer (*2*), bubble point curves as a function of temperature, at constant composition, are obtained for the pure components and certain mixtures. The data can be represented by Antoine-type equations,

$$\log \pi = b_0 - \frac{b_1}{b_2 + t} \tag{3}$$

or for greater pressure ranges,

$$\log \pi = b_0 + \frac{b_1}{t} + \frac{b_2}{t^2} + \ldots \tag{4}$$

and the total pressures as a function of composition calculated at predetermined constant temperatures. The excess pressures can be calculated and represented by an empirical function of the form,

$$P_{12}^E = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{5}$$

A rather sensitive and revealing plot of the experimental data is (P_{12}^E/x_1x_2) *vs.* $(x_1 - x_2)$, which readily suggests the probable degree of the polynomial (Equation 5) required to represent the data. The constants in the equation can be obtained by a standard curve-fitting procedure—e.g., the IBM program H-830 for IBM 650 digital computer, or a hand calculator procedure. Usually 2 to 4 constants will produce a good representation and satisfy the experimental accuracy.

The first step in the sequence of calculations is to obtain π, and $\left(\frac{\partial \pi}{\partial x_i}\right)_T$,

$$\pi = x_1 p_1^\circ + p_2^\circ + P_{12}^E \tag{6}$$

$$\left(\frac{\partial \pi}{\partial x_1}\right) = p_1^\circ - p_2^\circ + \left(\frac{\partial P_{12}^E}{\partial x_1}\right) \tag{7}$$

Differentiating Equation 5 gives,

$$\left(\frac{\partial P_{12}^E}{\partial x_1}\right) = -\left(\frac{x_1 - x_2}{x_1 x_2}\right) P_{12}^E + 2x_1x_2 \sum_i i a_i (x_1 - x_2)^{i-1} \tag{8}$$

From the standpoint of thermodynamics the total equilibrium pressure is given by

$$\pi = \sum x_i \gamma_i P_i \tag{9}$$

where

$$P_i = \left(\frac{p_i^\circ \nu_i^\circ}{\nu_i}\right) e^{\frac{V_{iL}(\pi - p_i^\circ)}{RT}} = p_i^\circ F_i \tag{10}$$

Then,

$$\pi = \sum x_i \gamma_i p_i^\circ F_i \tag{11}$$

The fugacity ratio correction term, F_i, can be calculated by an appropriate equation of state, the complexity of which will depend on the magnitude of the pressure.

Over the range π = 0 to 1500 mm. of Hg absolute a simplified form of the Redlich-Kwong (*6*) equation can be used as follows:

$$\ln\nu_i^\circ = (B_i - A_i^2)\, p_i^\circ \tag{12}$$

$$\ln\nu_i = [B_i - A_i^2 + (A_i - A_m)^2]\, \pi \tag{13}$$

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[1] Deceased.

$$A_i = \left(\frac{0.6541\, T_{ci}^{\ 1.25}}{P_{ci}^{\ .5} T^{1.25}} \right) \quad ; \qquad B_i = \left(\frac{0.0867\, T_{ci}}{P_{ci} T} \right) \tag{14}$$

$$A_m = \sum_i \ y_i A_i \qquad ; \qquad B_m = \sum_i \ y_i B_i \tag{15}$$

In Equations 12, 13, 14, and 15 all pressures are in atmospheres.

For binary systems Equation 11 can be written

$$\pi = x_1 \gamma_1 P_1 + x_2 \gamma_2 P_2 \tag{16}$$

and differentiated. Inserting the Gibbs-Duhem relationship gives

$$\left(\frac{\partial \pi}{\partial x_1} \right) = \left[x_1 \left(\frac{\partial \gamma_1}{\partial x_1} \right) + \gamma_1 \right] \left(P_1 - P_2 \ \frac{\gamma_2}{\gamma_1} \right) \tag{17}$$

$$\left(\frac{\partial \pi}{\partial x_1} \right) = \left[\gamma_2 - x_2 \ \left(\frac{\partial \gamma_2}{\partial x_1} \right) \right] \left(\frac{\gamma_1}{\gamma_2} \ P_1 - P_2 \right) \tag{17a}$$

Equations 16 and 17 could be solved simultaneously at a given composition for γ_1 and γ_2 except for the fact that $(\partial \gamma_1 / \partial x_1)$ is not known initially.

Several methods of varying degrees of approximation can be used to calculate the activity coefficient slopes. The Redlich-Kister-Turnquist (*5*) activity coefficient functions can be used.

$$\log \gamma_1 = x_2^2 [B + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2) + \ldots] \tag{18}$$

$$\log \gamma_2 = x_1^2 [B + C(x_1 - 3x_2) + D(x_1 - x_2)(x_1 - 5x_2) + \ldots] \tag{19}$$

$$\left(\frac{\partial \gamma_1}{\partial x_1} \right) = -4.6052\ \gamma_1 [B x_2 - 3C(x_2^2 - x_1 x_2) \ldots] \tag{20}$$

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right) = 4.6052\ \gamma_2 [B x_1 - 3C(x_1 x_2 - x_1^2) \ \ldots] \tag{21}$$

As first approximations,

$$\left(\frac{\partial \gamma_1}{\partial x_1} \right)^{(1)} = -4.6052\ \gamma_1 B x_2 = \frac{-4.6052\ \gamma_1 \log \gamma_1}{x_2} \tag{22}$$

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right)^{(1)} = +4.6052\ \gamma_2 B x_1 = \frac{4.6052\ \gamma_2 \log \gamma_2}{x_1} \tag{23}$$

Further, in the region $x_1 = 0 \rightarrow 0.10$,

$$\left(\frac{\partial \gamma_2}{\partial x_1} \right) \cong \frac{2(\gamma_2 - 1)}{x_1} \tag{24}$$

and similarly in the region $x_1 = 0.90 \rightarrow 1.0$

$$\left(\frac{\partial \gamma_1}{\partial x_1} \right) \cong \frac{-2(\gamma_1 - 1)}{x_2} \tag{25}$$

The difference between Equations 18 and 19 gives an equation for $\log(\gamma_1/\gamma_2)$ which can be used at two points (a and b) to obtain values for B and C:

$$C = \left[\frac{\log \left(\frac{\gamma_1}{\gamma_2} \right)_a - \frac{(x_2 - x_1)_a}{(x_2 - x_1)_b} \log \left(\frac{\gamma_1}{\gamma_2} \right)_b}{(6x_1x_2 - 1)_a - \frac{(x_2 - x_1)_a}{(x_2 - x_1)_b} (6x_1x_2 - 1)_b} \right] \tag{26}$$

$$B = \left[\frac{\log (\gamma_1/\gamma_2)_a - (6x_1x_2 - 1)\, C}{(x_2 - x_1)_a} \right] \tag{27}$$

Values calculated can be used in Equations 20 and 21 to obtain intermediate values of the slopes $(\partial \gamma_1 / \partial x_1)$ and $(\partial \gamma_2 / \partial x_1)$.

The excess free energy values can be calculated from γ-values by Equations 2a, and represented by the empirical series previously proposed (*5*):

$$\left(\frac{F_x^E}{2.303RT} \right) = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 \ldots] \tag{28}$$

CALCULATIONAL PROCEDURE

Based on the foregoing mathematical equations the sequence of calculations presented by Figure 1 can be pursued. Once the experimental data have been reduced to values of x_1, π, and P_{12}^E at constant temperature, a plot of $(P_{12}^E / x_1 x_2)$ *vs.* $(x_1 - x_2)$ is useful in determining the degree of Equation 5.

Vapor Phase Corrections. Via the adjusted vapor pressures P_1 and P_2 must be corrected prior to calculation of the excess free energy. For this purpose, as indicated by Equation 15, the vapor composition is required which is not available initially; fortunately, certain simplifying assumptions can be made which lead to a direct solution of the equations, and of sufficient accuracy to obtain P_1 and P_2. The following procedure is suggested.

At predetermined values of x_1, π and $(\partial \pi / \partial x_1)$ can be calculated by Equations 6 and 7.

At $x_1 = 0.05$ and 0.95, γ_1 and γ_2 can be calculated using Equation 16, 17, or 17a, and assuming $(\partial \gamma_2 / \partial x_1)$ and $(\partial \gamma_1 / \partial x_1)$ are negligible at the respective x_1 values.

Using the foregoing, γ_1 and γ_2 values at the "two points" in question, B and C, can be calculated by Equations 26 and 27, and following this γ's and y's calculated at the predetermined values of x_1.

Next, A_1, B_1, A_2, B_2, A_m, B_m, $\nu_1°$, ν_1, $\nu_2°$, ν_2 and P_1 and P_2 are calculated by Equations, 14, 15, 12, 13, and 10.

To facilitate the calculations, the x_1 axis is divided into regions as indicated by Figure 2.

Region 1, $x_1 = 0 \rightarrow 0.10$. In region 1, $(\partial \gamma_2 / \partial x_1)$ is very small and can be represented satisfactorily by Equation 24; consequently, 16 and 17a can be solved simultaneously to give

$$\gamma_1 = + \frac{\beta}{2\alpha} \pm \left[\left(\frac{\beta}{2\alpha} \right)^2 - \frac{\eta}{\alpha} \right]^{1/2} \tag{29}$$

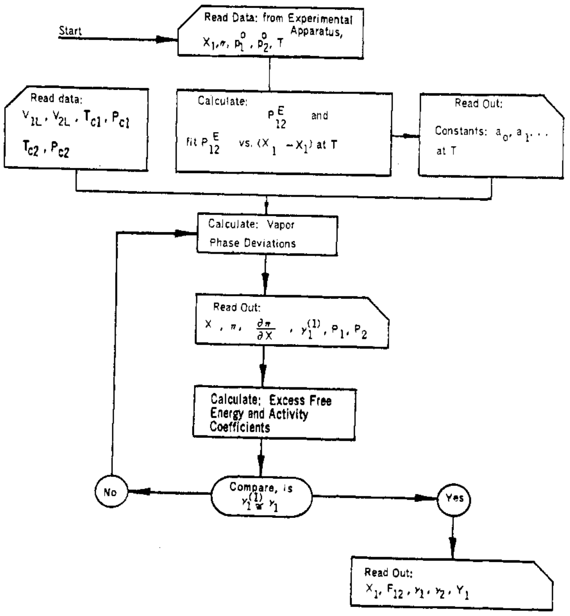

Figure 1. Calculational sequence

$$\gamma_2 = \left(\frac{\pi - x_1\alpha_1 P_1}{x_2 P_2}\right) \tag{30}$$

where

$$\alpha = x_1\left(1 - \frac{2x_2}{x_1}\right)\left(1 + \frac{x_1}{x_2}\right)P_1^2 \tag{31}$$

$$\nu = \pi\left[\frac{\partial\pi}{\partial x_1} + \frac{2x_2P_2}{x_1} + \frac{\pi}{x_2}\left(1 - \frac{2x_2}{x_1}\right)\right] \tag{32}$$

$$\beta = \left(\frac{\alpha\pi}{x_1P_1} + \frac{\eta x_1 P_1}{\pi} + \frac{2x_2^2P_2P_1}{x_1}\right) \tag{33}$$

Region 2, x_1 = 0.90 → 1.00. In this region, in a similar manner, using Equations 16, 17, and 25 the activity coefficients can be determined:

$$\gamma_2 = \frac{\beta'}{2\alpha'} \pm \left[\left(\frac{\beta'}{2\alpha'}\right)^2 + \frac{\eta'}{\alpha'}\right]^{1/2} \tag{34}$$

$$\gamma_1 = \left(\frac{\pi - x_2\gamma_2P_2}{x_1P_1}\right) \tag{35}$$

where

$$\alpha' = x_2\left(1 - \frac{2x_1}{x_2}\right)\left(1 + \frac{x_2}{x_1}\right)P_2^2 \tag{36}$$

$$\eta' = \pi\left[\left(\frac{\partial\pi}{\partial x_1}\right) - \frac{2x_1}{x_2}P_1 - \frac{\pi}{x_1}\left(1 - \frac{2x_1}{x_2}\right)\right] \tag{37}$$

$$\beta' = \left[\frac{\alpha'\pi}{x_2P_2} - \frac{\eta' x_2P_2}{\pi} + \frac{2x_1^2P_2\mathrm{P}_1}{x_2}\right] \tag{38}$$

Region 3, x_1 ≅ 0.35 → 0.65. The point at which $\gamma_1 = \gamma_2$, crossover point, falls in this region and usually is in the range of x_1 indicated. The mathematical technique used is based on finding this unique point. $\gamma_1 = \gamma_2 = \gamma_3$ can be substituted into Equations 16 and 17, giving

$$\gamma_e = \left(\frac{\pi}{x_1P_1 + x_2P_2}\right) \tag{39}$$

$$\gamma_e = \left(\frac{1}{P_1 - P_2}\right)\left(\frac{\partial\pi}{\partial x_1}\right) - x_1\left(\frac{\partial\gamma_1}{\partial x_1}\right) \tag{40}$$

A difference function (between Equations 39 and 40) can be written,

$$D(x) = \left(\frac{\pi}{x_1P_1 + x_2P_2}\right) - \left(\frac{1}{P_1 - P_2}\right)\left(\frac{\partial\pi}{\partial x_1}\right) + x\left(\frac{\partial\gamma_1}{\partial x_1}\right) \tag{41}$$

$$D(x) = \left(\frac{\pi}{x_1P_1 + x_2P_2}\right)\left[1 - \frac{4.6052\,x_1}{x_2}\log\frac{\pi}{(x_1P_1 + x_2P_2)}\right] - \left(\frac{\partial\pi}{\partial x_1}\right)\left(\frac{1}{P_1 - P_2}\right) \tag{42}$$

A search of the region can be made until $D(x) = 0$ is found; if adjustment of $(\partial\gamma_1/\partial x_1)$ in Equation 41 is required, additional approximations can be made, finally converging on the correct $D(x) = 0$.

Region 4, x_1 = 0.10 → 0.60. Equations 16, 17, or 17a, 20, or 21 can be solved for the activity coefficients giving,

$$\gamma_2 = \left[\frac{\frac{\pi}{x_1} - \left(\frac{1}{1 - gx_1}\right)\left(\frac{\partial\pi}{\partial x_1}\right)}{P_2\left(1 + \frac{x_2}{x_1}\right)}\right] \tag{43}$$

$$\gamma_1 = \left(\frac{\pi - x_2\gamma_2P_2}{x_1P_1}\right) \tag{44}$$

where

$$g = 4.6052[Bx_2 + 3Cx_2(x_1 - x_2)] \tag{45}$$

B and C can be calculated from Equations 26 and 27 using points $x_1 = 0.10$ and $x_1 = x_e$.

Region 5, x_1 = 0.40 → 0.90. In a similar manner, in this region,

$$\gamma_1 = \left[\frac{\left(\frac{1}{1 - gx_1}\right)\left(\frac{\partial\pi}{\partial x_1}\right) + \frac{\pi}{x_2}}{P_1\left(1 + \frac{x_1}{x_2}\right)}\right] \tag{46}$$

$$\gamma_2 = \left(\frac{\pi - x_1\gamma_1P_1}{x_2P_2}\right) \tag{47}$$

and B and C determined using $x_1 = x_e$ and 0.90.

Excess Free Energy. Values at the predetermined values of x_1 can be calculated by Equation 2a, followed by a least squares representation using Equation 28. This smoothing automatically gives the activity coefficients by Equations 18 and 19 and hence the final tabular values of γ_1, γ_2, and y_1. If the least squares representation by Equation 28 requires more than two constants, another set of calculations can be made using slopes calculated from Equations 20 and 21, to arrive at the final set of values.

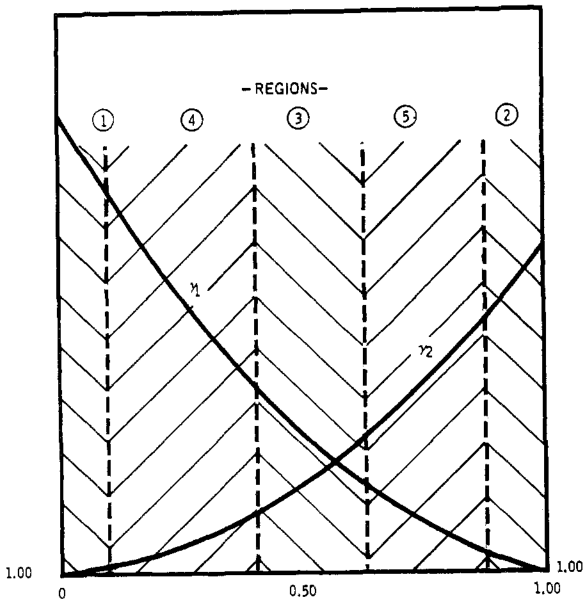

Figure 2. Regions for calculational purposes

CALCULATION OF EXPERIMENTAL DATA

To illustrate results obtainable by the calculational procedure, three systems with greatly different excess free energies have been chosen.

Carbon Tetrachloride–Cyclohexane. Scatchard, Wood, and Mochel (7) made vapor-liquid measurements on this system over a temperature range of 30° to 70° C. Since an equilibrium still was used, the vapor composition also was determined in addition to x_1, π, and T. Other thermodynamic properties and F_{12}^E were calculated from the data.

From the data reported at 40° C., without recourse to the y-values, the excess free energy and activity coefficients were calculated, and are summarized in Table I. Figure 3,

Table I. Carbon Tetrachloride–Cyclohexane

Experimental Data			Calculated Data[a]						
CCl_4 X_1	π mm. hg.	P^E_{12}	X_1	P_1	P_2	F^E_{12}	γ_1	γ_2	y_1
0.0000	184.61 = p°_2	0.00	0.0000	213.08	184.61	0.000	1.1028	1.0000	0
0.1262	190.62	2.38	0.1000	213.12	184.65	5.527	1.0841	1.0009	0.1220
0.2453	195.62	3.96	0.2000	213.16	184.69	9.919	1.0672	1.0037	0.2348
0.3669	200.08	4.93	0.3000	213.19	184.72	13.12	1.0520	1.0086	0.3404
0.4739	203.40	5.18	0.4000	213.23	184.75	15.12	1.0386	1.0155	0.4404
0.4753	203.45	5.18	0.5000	213.25	184.78	15.88	1.0271	1.0248	0.5364
0.5151	204.59	5.18	0.6000	213.28	184.80	15.38	1.0175	1.0366	0.6295
0.6061	206.97	4.95	0.7000	213.30	184.82	13.60	1.0102	1.0510	0.7214
0.7542	210.15	3.87	0.8000	213.32	184.84	10.48	1.0045	1.0684	0.8635
0.8756	212.04	2.27	0.9000	213.33	184.85	5.958	1.0012	1.0889	0.9052
1.0000	213.34 = p°_1	0.00	1.0000	213.34	184.86	0.000	1.0000	1.1130	1.0000

[a] Critical constants: T_{c1} = 556.36° K., P_{c1} = 45.0 atm.; T_{c2} = 554.27; P_{c2} = 40.4: P^E_{12} constants: $a_0 = 20.828$, $a_1 = -0.5228$, $a_2 = +0.8498$; Liquid Volumes: $V_{1L} = 0.099702$; $V_{2L} = 0.11082$. Activity coefficient constants: $B = 0.04449$; $C = 0.00198$.

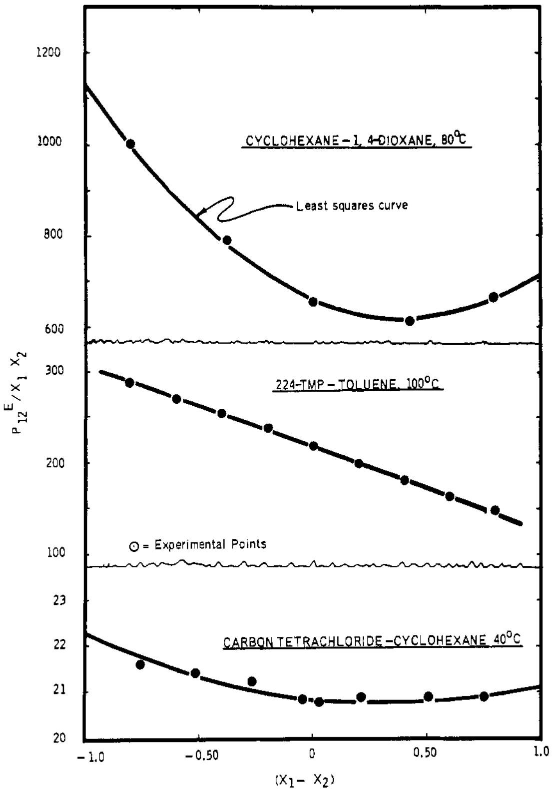

Figure 3. Excess pressure values
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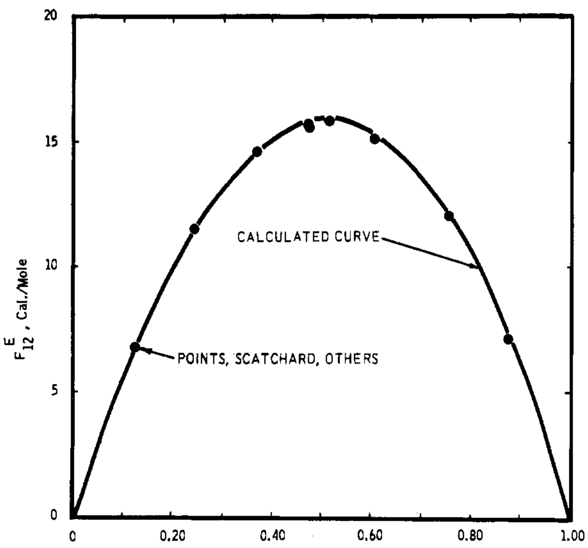

Figure 4. Comparison of F^E_{12} for carbon tetrachloride–cyclohexane at 40° C.

Table II. 2,2,4-Trimethylpentane–Toluene at 100° C.

Experimental Data			Calculated Data[a]					
(2,2,4 TMP) x_1	π	P^E_{12}	P_1	P_2	F^E_{12}	γ_1	γ_2	y_1
0.0000	556.3 = p°_2	0	769.33	556.3	0	1.4051	1.0000	0.0000
0.1000	604.3	25.97	770.64	557.20	21.63	1.2938	1.0043	0.1650
0.2000	643.6	43.24	772.00	557.92	35.77	1.2085	1.0170	0.2899
0.3000	676.0	53.61	773.10	558.50	46.76	1.0445	1.0360	0.3584
0.4000	702.0	57.58	773.98	558.95	53.57	1.0948	1.0600	0.4828
0.5000	721.3	54.85	774.67	559.29	55.83	1.0591	1.0888	0.5687
0.6000	736.2	47.72	775.22	559.54	52.21	1.0338	1.1213	0.6532
0.7000	74.84	37.89	775.64	559.72	43.18	1.0170	1.1560	0.7378
0.8000	758.5	25.96	776.00	559.86	30.38	1.0066	1.1920	0.8239
0.9000	767.9	13.33	776.30	559.96	15.49	1.0014	1.2261	0.9111
1.0000	776.6 = p°_1	0	776.6	560.04	0	1.0000	1.2581	1.0000

[a] Critical constants. T_{c1} = 544.1° K. P_{c1} = 25.4 atm.; T_{c2} = 593.8, P_{c2} = 41.6. P^E_{12} constants $a_0 = 218.12$ $a_1 = -89.74$; liquid volumes: $V_{1L} = 0.18367$; $V_{2L} = 0.11617$. Activity coefficient constants: $B = 0.1237$, $C = -0.0240$.

Table III. Cyclohexane–1,4-Dioxane at 80° C.

Experimental Data			Calculated Data[a]						
C_6H_{12}, x_1	π	P^E_{12}	x_1	P_1	P_2	F^E_{12}	γ_1	γ_2	y_1
0.0974	504.46	87.91	0.0000	734.91	381.28	0	2.5539	1.0000	0.0000
			0.1000	737.45	382.79	59.38	2.1735	1.0078	0.3158
0.3100	662.21	168.71	0.2000	739.61	383.84	105.9	1.8828	1.0309	0.4681
			0.3000	741.10	384.57	140.2	1.6481	1.0739	0.5589
0.5010	726.97	164.32	0.4000	742.14	385.08	160.3	1.4686	1.1325	0.6249
			0.5000	742.89	385.44	168.4	1.3282	1.2165	0.6779
0.7110	765.46	126.80	0.6000	743.43	385.70	166.5	1.2116	1.3569	0.7208
			0.7000	743.81	385.88	151.5	1.1147	1.5938	0.7588
0.8950	767.56	62.30	0.8000	743.98	385.97	117.8	1.0449	1.9416	0.8059
			0.9000	743.86	385.90	66.10	1.0096	2.3527	0.8816
			1.0000	743.28	385.60	0	1.0000	2.8700	1.0000

[a] Critical constants: $T_{c1} = 554.27°$ K.; $P_{c1} = 40.4$ atm.; $T_{c2} = 585.16$, $P_{c2} = 50.7$. P^E_{12} constants. $a_0 = 662.1$; $a_1 = 210.9$; $a_2 = 264.4$; $V_{1L} = 0.11688$; $V_{2L} = 0.09134$. Activity coefficient constants: $B = 0.4225$, $C = 0.0338$, $D = 0.0185$.

a plot of (P^E_{12}/x_1x_2), shows the experimental points and the least squares curve. Figure 4 shows the calculated excess free energy curve along with the values of Scatchard, Wood, and Mochel.

2,2,4-Trimethylepentane–Toluene. Data for this system at 100° C., calculated by the cut-and-try curve fit method with a hand calculator, have been reported (2). The same set of data, presented in Figure 3 and Table II, has been recalculated by the method proposed herein and the results presented in Table II. We consider these results to be more correct than those published previously.

Cyclohexane–1,4-Dioxane. Measurements on this system have been made recently in these laboratories (3), and the set of data at 80° C. is given in Table III, along with the calculated results. The excess pressure function is presented in Figure 3.

The foregoing illustrates that the calculation of the excess free energy and activity coefficients from excess pressure data, without knowledge of the vapor composition, is possible by a method readily adaptable to automatic machine computation. Furthermore the results are comparable to those obtainable by direct calculation where the vapor composition is known.

NOMENCLATURE

A_i, A_m = constants in Redlich-Kwong equation of state; i refers to ith component and m to mixture
$B, C, D, \ldots$ = constants in Equations, 18, 19, and 28
B_i, B_m = constants in Redlich-Kwong equation of state
$D(x)$ = special difference function defined by Equation 41
F^E_x = excess free energy
F_i = fugacity coefficient correction ratio
P = adjusted vapor pressure
P_c = critical pressure
P^E_{12} = excess pressure
R = gas constant
T = temperature, ° K.; T_c = critical temperature, ° K.
V_L = molal liquid volume
$a_0, a_1, a_2, \ldots$ = constants in excess pressure function
$b_0, b_1, \ldots$ = vapor pressure equation constants
g = special function defined by Equation 45
$p°$ = vapor pressure
t = temperature, ° C.
x = liquid phase mole fraction
y = vapor phase mole fraction
α, α' = parameters defined by Equations 31 and 36.
β, β' = parameters defined by Equations 33 and 38.
γ = activity coefficient
η, η' = parameters defined by Equations 32 and 37
$\nu, \nu°$ = fugacity coefficients, at mixture conditions and pure component conditions, respectively
π = total pressure

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