Vapor-Liquid Equilibrium:

Part III. Data Reduction with Precise Expressions for G^E

Through an empirical but rational approach to the development of equations to represent the composition dependence of the excess Gibbs function for binary liquid systems, it has been found possible to correlate VLE data precisely, even for highly nonideal systems. This makes possible the application of Barker's method to the reduction of VLE data on a routine basis. The validity of the method is demonstrated through application to several sets of data from the literature, and new experimental data are presented for six diverse binary systems in vapor-liquid equilibrium at 50°C.

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SCOPE

In Part I of this series of papers Van Ness et al. (1973) described the numerical methods by which one may accomplish the reduction of binary VLE data to yield a correlation for the excess Gibbs function of the liquid phase. Byer et al. (1973) in Part II demonstrated the effectiveness of the numerical procedure based on P-x data alone for 15 binary systems. There is an additional procedure for the reduction of P-x data, developed by Barker (1953), that was not pursued in these earlier papers. It is based on Equation (15) of the present paper, an exact thermodynamic expression relating the vapor pressure of a liquid solution to its composition and to the excess Gibbs function. If G^E is replaced in this equation by an analytical expression that gives its composition dependence, then one has an equation for vapor pressure as a function of liquid composition, and any number of unknown parameters in the expression for G^E can be determined from P vs. x data by regression. The only difficulty is that one must always have at hand an appropriate expression for G^E as a function of x. Of the 15 systems reported by Byer et al. in Part II only one showed such large deviations from ideality that it could not be characterized by the four-suffix Margules equation. In fact, the data for this system, n-pentanol-n-hexane, defied representation within the precision of the data by all known equations. It was the existence of such highly nonideal systems that deterred us from the exploitation of Barker's method as a general procedure for the reduction of P-x data. However, Barker's method is a most attractive one-step fitting procedure, and this fact provides the incentive for development here of the means by which it can be made more generally applicable.

CONCLUSIONS AND SIGNIFICANCE

We have found that highly nonideal systems, even those verging on instability, may be very precisely fit by one of two simple equations, the 5-suffix Margules equation or a new equation called the modified Margules equation. Both are basically four-parameter equations that reduce to the three- and four-suffix Margules equations as special cases. Thus they retain all of the advantages associated with the Margules equations, including the capability of predicting limited liquid-liquid miscibility. Applied to data from the literature for the methanol-carbon tetrachloride and chloroform-ethanol systems these equations are shown to yield very precise correlations of the P-x-y data when regression is carried out by Barker's method, which is based on just the P-x data. From this we conclude that reliable P-x data only are required to provide reliable VLE relationships. Moreover, it is shown that use of the reported y values along with the P-x data in the data-reduction process distorts the correlation of both the P-x and y-x relationships. Barker's method in conjunction with the two types of Margules equations mentioned earlier are applied in the correlation of new VLE data at 50°C for the binary systems acetone-chloroform, acetone-methanol, chloroform-methanol, chloroform-ethanol, chloroform-n-heptane, and ethanol-n-heptane. These systems were investigated as part of a larger study of the ternary systems acetone-chloroform-methanol and chloroform-ethanol-n-heptane to be reported in Part IV of this series of papers.

In Part II of this series of papers on vapor-liquid equilibrium (VLE), Byer et al. (1973) reported data for 15 binary systems at 30°C and found that for 14 of these systems the data (P vs. x) were correlated to within the limits of experimental uncertainty through use of the four-suffix Margules equation. On the other hand, none of the currently used G^E vs. x expressions served to represent the data for n-pentanol-n-hexane to within experimental precision. The inadequacy of these equations in the representation of precise data for certain complex mixtures has prompted us in the past to rely on numerical techniques for data reduction (Van Ness et al., 1973).

However, Barker's method for the reduction of P-x data (Barker, 1953) is in principle a more attractive procedure because it is a single-step analytical fitting technique that makes direct use of the measured data. Furthermore, it is applicable to multicomponent as well as to binary systems. The only requirement is the availability of an analytical expression representing G^E as a function of x that is capable of producing a fit to the data within the limits of experimental uncertainty. Our purpose here is to describe an empirical approach taken to meet this requirement and to demonstrate its success.

EQUATION DEVELOPMENT

The quantity g/x_1x_2 and its reciprocal x_1x_2/g where $g \equiv G^E/RT$, serve as vehicles for model discrimination when considered as functions of x (Van Ness, 1964). Thus when g/x_1x_2 vs. x is linear, the system is described by the 3-suffix Margules equation:

$$\frac{g}{x_1x_2} = A_{21}x_1 + A_{12}x_2 \qquad (1)$$

When x_1x_2/g vs. x is linear, we have the van Laar equation:

$$\frac{x_1x_2}{g} = \frac{x_1}{A_{21}} + \frac{x_2}{A_{12}} \qquad (2)$$

Equations (1) and (2) have been widely used, and their capabilities and shortcomings are well known. Although neither is in general satisfactory for application to highly nonideal solutions, both represent possible bases for further development. In the following treatment we exploit this possibility by letting Equations (1) and (2) represent standards of reference to which the actual g vs. x behavior of a solution may be compared. Thus, with respect to Equation (1) we define a special function g(net), given as the difference between values of g/x_1x_2 predicted by the linear relation of Equation (1) and values determined by experiment:

$$g(\text{net}) \equiv A_{21}x_1 + A_{12}x_2 - \frac{g}{x_1x_2} \qquad (3)$$

Similarly, with respect to Equation (2) we define the function $\tilde{g}$ (net), given by

$$\tilde{g}\ (\text{net}) \equiv \frac{x_1}{A_{21}} + \frac{x_2}{A_{12}} - \frac{x_1x_2}{g} \qquad (4)$$

If we arbitrarily specify that g(net) and $\tilde{g}$ (net) be identically zero at $x_1 = 0$ and $x_1 = 1$, then the graphical interpretation of these functions is as shown in Figure 1.

The functions g(net) and $\tilde{g}$ (net) are in some respects analogous to g. Thus, as with g, these functions result from a comparison of an actual solution property with the same property as predicted on the basis of some standard of behavior. Plots of g(net) and $\tilde{g}$ (net) vs. x_1 are similar in shape to plots of g vs. x_1, going to zero at $x_1 = 0$ and $x_1 = 1$ and exhibiting an extremum at an intermediate composition. Thus, plots of $g(\text{net})/x_1x_2$ and $\tilde{g}$ $(\text{net})/x_1x_2$ or their reciprocals vs. x_1 can be expected to resemble plots of g/x_1x_2 or its reciprocal vs. x_1. In particular, one would hope to find that data for a number of complex systems would yield plots approaching linearity on one or more of these graphs, thus providing convenient correlating relationships. Consideration of a number of systems for which the data have proved resistant to precise correlation yields the result that one or the other of the two plots based on Equation (3), and related to the 3-suffix Margules equation, is found to be essentially linear.

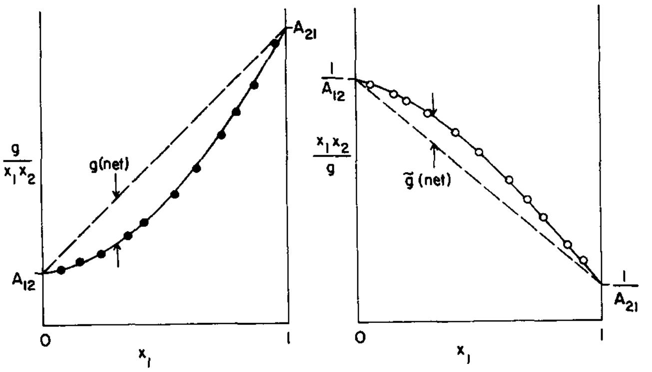

Fig. 1. Graphical interpretation of *g(net)* and *g(net)*.

The linear relation between $g(\text{net})/x_1x_2$ and x_1 can be expressed as

$$g(\text{net}) = (\lambda_{21}x_1 + \lambda_{12}x_2)x_1x_2$$

Combining this with Equation (3), we get

$$\frac{g}{x_1x_2} = A_{21}x_1 + A_{12}x_2 - (\lambda_{21}x_1 + \lambda_{12}x_2)x_1x_2 \qquad (5)$$

This is in fact the 5-suffix Margules equation; although known for many years, it has rarely been applied. The alternative correlation, expressing the linearity of $x_1x_2/g(\text{net})$ with x_1, can be written

$$\frac{x_1x_2}{g(\text{net})} = \frac{x_1}{\alpha_{21}} + \frac{x_2}{\alpha_{12}}$$

or

$$g(\text{net}) = \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2}$$

In combination with Equation (3) this gives

$$\frac{g}{x_1x_2} = A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2}$$

Experience has shown that the fit provided by this equation can sometimes be enhanced by the addition of a fifth parameter:

$$\frac{g}{x_1x_2} = A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2} \qquad (6)$$

No equation of this form appears in the literature; we call it the modified Margules equation.

Equations (5) and (6) taken together provide great flexibility in the fitting of VLE data and have yielded correlations within experimental precision for all of the highly nonideal systems we have examined. Both equations have the advantage of algebraic simplicity, and both include as special cases the 3- and 4-suffix Margules equations. Thus if $\lambda_{12} = \gamma_{21} = D$ in Equation (5) or if $\alpha_{12} = \alpha_{21} = D$ and $\eta = 0$ in Equation (6), both reduce to the 4-suffix Margules equation:

$$\frac{g}{x_1x_2} = A_{21}x_1 + A_{12}x_2 - Dx_1x_2 \qquad (7)$$

This equation was treated in detail in Parts I and II of this series of papers (Van Ness et al., 1973; Byer et al., 1973), where it was shown to be capable of representing faithfully the observed G^E behavior of many systems.

The expressions for $\ln \gamma_1$ and $\ln \gamma_2$ consistent with Equation (5), the 5-suffix Margules equation, are given as

$$\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1 + 2(\lambda_{21}x_1 + \lambda_{12}x_2)x_1(x_1 - x_2) - \lambda_{21}x_1^2] \quad (8a)$$

$$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2 + 2(\lambda_{21}x_1 + \lambda_{12}x_2)x_2(x_2 - x_1) - \lambda_{12}x_2^2] \quad (8b)$$

The corresponding expressions with respect to Equation (6), the modified Margules equation, are

$$\ln \gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2} + \frac{\alpha_{12}\alpha_{21}(\alpha_{12} + \eta x_2^2)x_1^2}{(\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2)^2}\right] \quad (9a)$$

$$\ln \gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2} + \frac{\alpha_{12}\alpha_{21}(\alpha_{21} + \eta x_1^2)x_2^2}{(\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2)^2}\right] \quad (9b)$$

With the exception of η, the parameters in these equations are directly related to the infinite-dilution behavior of a solution. Thus for either the 5-suffix Margules equation or the modified Margules equation

$$A_{12} = \ln \gamma_1^\infty = \left(\frac{g}{x_1x_2}\right)_{x_1=0} \quad (10a)$$

$$A_{21} = \ln \gamma_2^\infty = \left(\frac{g}{x_1x_2}\right)_{x_1=1} \quad (10b)$$

The λ parameters in Equation (5) and the α parameters in Equation (6) also have exactly the same significance. Thus, it is readily shown that

$$\left.\begin{matrix}\lambda_{12}\\ \text{or}\\ \alpha_{12}\end{matrix}\right\} = A_{21} - 2A_{12} - \frac{1}{2}\left(\frac{d\ln\gamma_1}{dx_1}\right)_{x_1=0} = A_{21} - A_{12} - \left[\frac{d(g/x_1x_2)}{dx_1}\right]_{x_1=0} \quad (11a)$$

and

$$\left.\begin{matrix}\lambda_{21}\\ \text{or}\\ \alpha_{21}\end{matrix}\right\} = A_{12} - 2A_{21} + \frac{1}{2}\left(\frac{d\ln\gamma_2}{dx_1}\right)_{x_1=1} = A_{12} - A_{21} + \left[\frac{d(g/x_1x_2)}{dx_1}\right]_{x_1=1} \quad (11b)$$

Geometrical interpretations of these parameters are shown on a plot of g/x_1x_2 vs. x_1 in Figure 2.

Values of γ_1^∞, γ_2^∞, $(d\ln\gamma_1/dx_1)_{x_1=0}$, and $(d\ln\gamma_2/dx_1)_{x_1=1}$ for use in Equations (10) and (11) may be found from the first and second derivatives of the P vs. x_1 curve at $x_1 = 0$ and $x_1 = 1$. The following equations apply when the vapor phase is assumed to be an ideal gas:

$$\gamma_1^\infty = \frac{1}{P_1^{\text{sat}}}\left[P_2^{\text{sat}} + \left(\frac{dP}{dx_1}\right)_{x_1=0}\right] \quad (12a)$$

$$\gamma_2^\infty = \frac{1}{P_2^{\text{sat}}}\left[P_1^{\text{sat}} - \left(\frac{dP}{dx_1}\right)_{x_1=1}\right] \quad (12b)$$

$$\left(\frac{d\ln\gamma_1}{dx_1}\right)_{x_1=0} = \frac{(d^2P/dx_1^2)_{x_1=0}}{2(dP/dx_1)_{x_1=0} + P_2^{\text{sat}}} \quad (13a)$$

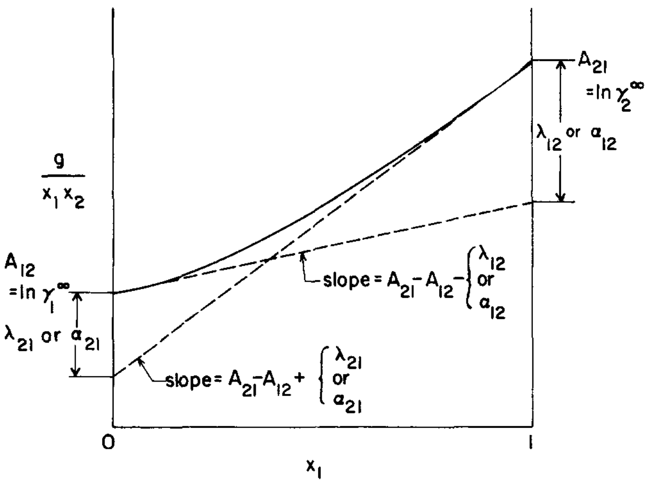

Fig. 2. Graphical interpretation of parameters.

$$\left(\frac{d\ln\gamma_2}{dx_1}\right)_{x_1=1} = \frac{(d^2P/dx_1^2)_{x_1=1}}{2(dP/dx_1)_{x_1=1} - P_1^{\text{sat}}} \quad (13b)$$

Where one has sufficient data to prepare a smooth P vs. x_1 curve, approximate values of the limiting derivatives may be obtained if quadratic expressions are fit to short portions of the curve near $x_1 = 0$ and $x_1 = 1$.

Values of the parameters in Equations (5) and (6) must ultimately be determined from a set of experimental data by regression. Equations (10) through (13) provide estimates that are appropriate as starting values.

The parameter η in Equation (6) is included for "fine tuning" in very special cases. In particular, certain systems are so nonideal as to be very close to instability with respect to phase-splitting, and the parameter η may be required so as to yield an equation that does not incorrectly predict instability. The effect of a finite value for η is to replace the original linear relation proposed for $x_1x_2/g(\text{net})$ vs. x_1 by a quadratic dependence. Clearly, further terms could be included to make the relationship higher ordered, but this has not proved necessary. Similarly, with respect to Equation (5), the quantity in parentheses could be written as $(\lambda_{21}x_1 + \lambda_{12}x_2 + \xi x_1x_2)$, corresponding to a quadratic dependence of $g(\text{net})/x_1x_2$ on x_1. Again, this has not been found necessary.

The two additional functions, $\tilde{g}\,(\text{net})/x_1x_2$ and its reciprocal, introduced as a result of Equation (4) and based on the van Laar equation, have not proved useful. However, they do round out the catalogue of empirical fitting functions, and systems may exist for which their use would be appropriate.

Our objective here is the precise analytical representation of the g vs. x behavior of binary liquid solutions so as to allow application of Barker's method in the reduction of P-x data taken in studies of VLE. No consideration has been given to the possible interpretation of the equations in relation to any theory of molecular interactions. Our concern is solely with the fit provided to the data. We are proposing two empirical equations, each containing basically four parameters, which together appear to meet our needs. Both are extensions of the four-suffix Margules equation, and both therefore inherit all the abilities of that equation to represent observed phenomena, for example, mixed (positive-negative) deviations from ideality, interior extrema in the activity coefficient curves, and liquid-liquid phase splitting. They provide remarkable flexibility in the fitting of data and are algebraically tractable. Thus it should be possible to incorporate them easily into existing computation schemes based on the four-suffix Margules equation.

APPLICATIONS

The general thermodynamic equations used in this work are the same as those presented in Part I (Van Ness et al., 1973), except for certain multiplying factors that provide for the inclusion of corrections for vapor-phase nonidealities and for the effect of pressure on liquid-phase fugacities. Recalling that $g \equiv G^E/RT$, we may write the following equations for an ij binary system:

$$g = x_i \ln \gamma_i + x_j \ln \gamma_j \tag{14}$$

and

$$P = \frac{x_i P_i^{\text{sat}}}{\Phi_i} \exp\left(g + x_j \frac{dg}{dx_i}\right) + \frac{x_j P_j^{\text{sat}}}{\Phi_j} \exp\left(g - x_i \frac{dg}{dx_i}\right) \tag{15}$$

where

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \Phi_i$$

and

$$\Phi_i = \exp \frac{(B_{ii} - V_i^L)(P - P_i^{\text{sat}}) + P y_j^2 \delta_{ij}}{RT}$$

Since the terms on the right-hand side of Equation (15) represent the partial pressures, y_iP and y_jP, the y's are calculated by division of the values of these terms by the calculated value of P. Barker's method is carried out through application of Equation (15) in conjunction with a correlating expression for g, here either Equation (5) or (6). The procedure is to seek through regression a set of values for the parameters in the correlating expression for g that minimizes the sum of squares of the differences between experimental values of P and the corresponding values calculated by Equation (15). Since the y_i's are not known initially, calculation of the Φ_i's requires an iterative process.

The data for n-pentanol(1)-n-hexane(2) at 30°C reported by Byer et al. (1973) in Part II could not be satisfactorily fit by any equation then known to us. A compromise fit by the Wilson equation yielded pressure deviations outside the range of experimental precision. We have therefore applied Equation (6) in the regression of Byer's data by Barker's method, giving equal weight to all data points. Virial coefficients calculated from the recent correlation of Tsonopoulos (1974) are

$$B_{11} = -5180 \text{ cm}^3/\text{mol}$$
$$B_{22} = -1860 \text{ cm}^3/\text{mol}$$
$$B_{12} = -1480 \text{ cm}^3/\text{mol}$$

The values determined for the parameters in Equation (6) are

$$A_{12} = 3.3670 \qquad A_{21} = 1.4115$$
$$\alpha_{12} = 14.9300 \qquad \alpha_{21} = 1.5768$$
$$\eta = 0.0$$

The deviations, $\Delta P \equiv P(\text{calculated}) - P(\text{experimental})$, resulting from the correlation are shown in Figure 3. Direct comparison can be made of this figure with Figure 7a of Part II (Byer et al., 1973), which is based on the Wilson equation. The comparison is summarized as follows:

	Root mean square ΔP, mm Hg	Max ΔP, mm Hg
Wilson equation	1.02	1.92
Equation (6)	0.22	0.44

The deviations from the Wilson equation are largely systematic, whereas those from Equation (6) scatter in a much more nearly random manner about zero.

The improvement in fit achieved by Equation (6) in comparison with the Wilson equation comes at the expense of two more parameters. In machine computation this is of no significance. The use of a curve-fitting procedure in the reduction of thermodynamic data requires a precision of fit within the limits of experimental uncertainty, as is provided in this case by Equation (6), but not by the Wilson equation.

In our earlier work (Byer et al., 1973) the data-reduction process was entirely numerical, requiring first a spline fit of the P vs. x data and then a numerical solution to Equation (15) for generation of y and g values. Here the same P vs. x data are regressed directly by Barker's method. The results of the two data reduction procedures show no significant differences. We have found Equation (6) entirely adequate for other alcohol-hydrocarbon systems and will present results for the ethanol-n-heptane system as a further example.

Where P-x data alone are measured (as is the case in our work), the only test of suitability of Equations (5) and (6) is the comparison of calculated pressures with experimental values. Given that the experimental values of P and x are reliable, a basic premise of our work is that the VLE relationships computed from the P-x data will also be reliable, provided that the P-x data are fit within the limits of experimental uncertainty. To test this premise, we have examined several sets of P-x-y data found in the literature. The first system considered is methanol(1)-carbon tetrachloride(2) at 35°C. Three sets of data are available: Scatchard et al. (1946), Missen (1956), and Paraskevopoulos (1959). This system is highly nonideal, verging on instability, and the g vs. x relation has never been adequately fit. None of the authors cited offered an equation to correlate all of his data. Rather, curve-splicing techniques were employed.

The three data sets were used in the following way: The data of Scatchard et al. and those of Missen, taken together, were fit to yield correlating parameters in Equation (6), whereas those of Paraskevopoulos were reserved for comparison with values computed from the final correlation. With data available for P, x, and y, a value of g can be calculated by Equation (14) for each experimental point, and a direct fit by Equation (6) can then be made.

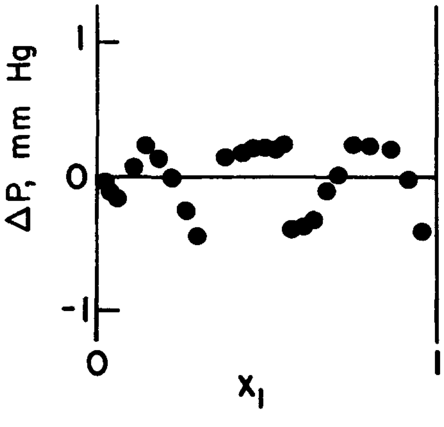

Fig 3. Deviations between calculated and experimental pressures: n-pentanol-n-hexane at 30°C.

Either g itself or g/x_1x_2 may be treated as the dependent variable, and we have done it each way with the data of both Scatchard and Missen, weighting all points equally in each case. For a given data set the values used for P_1^{sat} and P_2^{sat} were those reported with that set.

An alternative procedure is to employ Barker's method, basing the correlation on just the P-x data through application of Equation (15). A problem arising here is that single values of P_1^{sat} and P_2^{sat} are required in Equation (15), whereas each data set has its own values for the pure-component vapor pressures. The values reported by the various authors are as follows:

	P_1^{sat}, mm Hg	P_2^{sat}, mm Hg
Scatchard et al. (1946)	209.15	174.47
Missen (1956)	208.8	173.6
Paraskevopoulos (1959)	207.5	174.4
Average	208.5	174.2

In order to put Scatchard's data and Missen's data on the same basis, we applied corrections to all reported values of P according to the equation:

$$\frac{\delta P}{P} = y_1 \frac{\delta P_1^{sat}}{P_1^{sat}} + y_2 \frac{\delta P_2^{sat}}{P_2^{sat}} \qquad (16)$$

where

$$\delta P_i^{sat} = P_i^{sat}(\text{average}) - P_i^{sat}(\text{reported})$$

This equation was discussed briefly at the end of Part I

TABLE 1. PARAMETERS IN EQUATION (6) FOR METHANOL(1)—CARBON TETRACHLORIDE(2) AT 35°C BY THREE FITTING PROCEDURES

Data of Scatchard et al. (1946) and Missen (1956).
Virial coefficients: $B_{11} = -1645$,
$B_{22} = -1500$, $B_{12} = -735$ cm³/mol

	Fitting procedure		
	g/x_1x_2 vs. x_1	g vs. x_1	P vs. x_1
A_{12}	4.5709	4.3949	3.7893
A_{21}	1.9603	1.9432	2.0738
α_{12}	59.8310	42.4010	15.4031
α_{21}	2.6762	2.3551	2.0953
η	14.7910	5.6538	4.7834
Root mean square ΔP, mm Hg	4.37	4.50	0.77
Root mean square Δy	0.0126	0.0131	0.0068
Data of Paraskevopoulos (1959)		Root mean square ΔP, mm Hg	2.03
		Root mean square Δy	0.0041

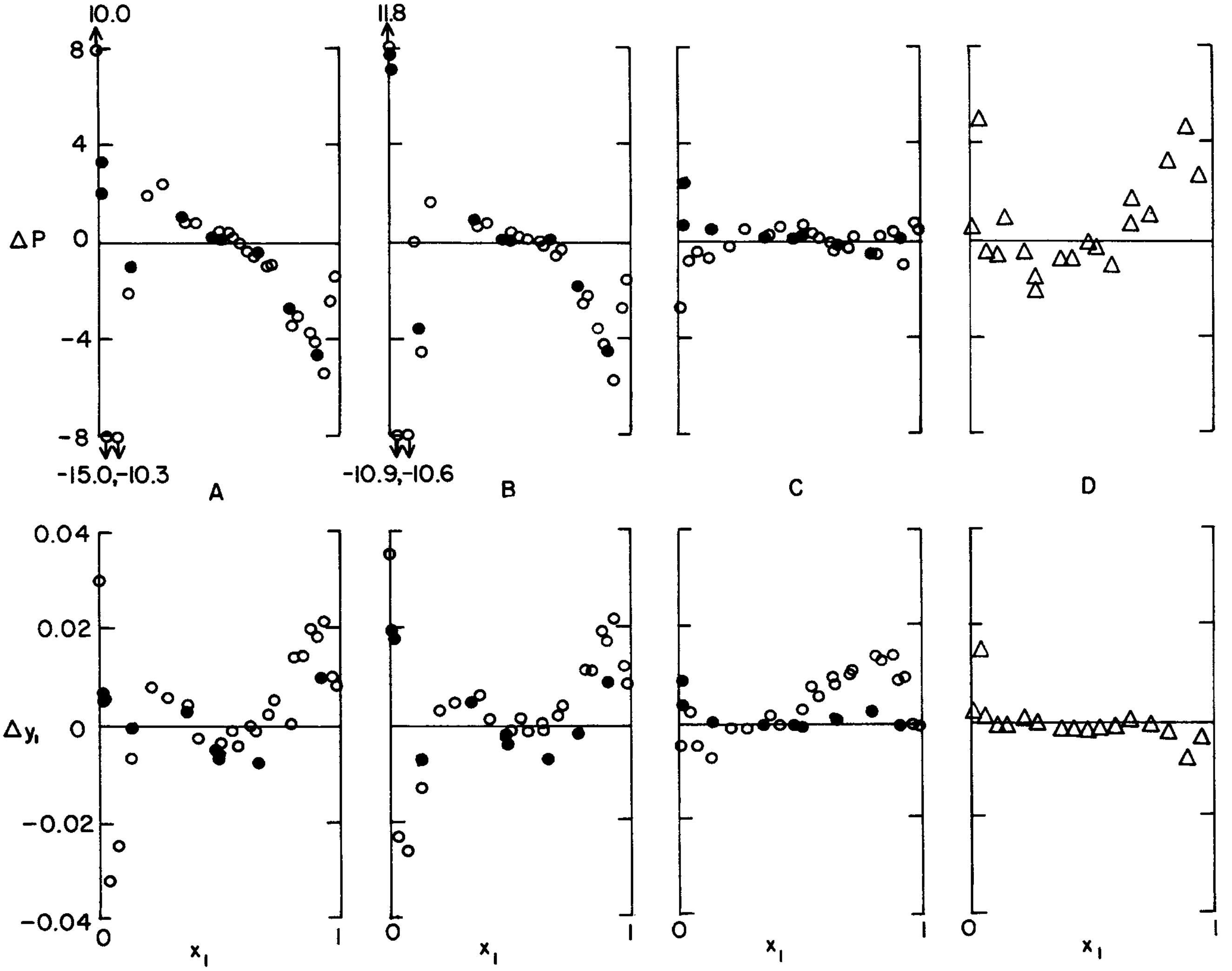

Fig. 4. ΔP(mm Hg) and Δy_1 vs. x_1 for methanol(1)-carbon tetrachloride(2) at 35°C: (A) based on fit of g/x_1x_2 vs. x_1; (B) based on fit of g vs. x_1; (C) based on fit of P vs. x_1; (D) based on fit of P vs. x_1, data not used in determination of correlation. ● Scatchard et al. (1946), ○ Missen (1956), △ Paraskevopoulos (1959).

(Van Ness et al., 1973). The values of P corrected in accord with Equation (16) were then used along with the average values of P_1^{sat} and P_2^{sat} in Equation (15) in the application of Barker's method. The justification for this procedure is that the parameters determined by regression are unchanged when an entire data set (including P_1^{sat} and P_2^{sat}) is shifted in accord with Equation (16).

The results of the three fitting procedures are summarized by Table 1 and displayed in Figure 4. The virial coefficients were determined from the correlation of Tsonopoulos (1974), as were all virial coefficients given in this paper. One sees from Table 1 that the parameters for Equation (6) depend on the fitting procedure, as does the quality of fit. The latter is indicated by the root mean square values given for ΔP and Δy but is seen most clearly from the plots of Figure 4. Plots A and B show the differences between calculated and experimental values of P and y for the two cases where all the experimental data (P, x, and y) were used in the determination of the parameters of the correlating equation. The nature of the fit depends very little on whether g or g/x_1x_2 is considered the dependent quantity, and the overall quality of the fit is about the same in the two cases: root mean square $\Delta P \simeq 4.4$ mm Hg and root mean square $\Delta y \simeq 0.013$. On the other hand, when only the P-x data are used in the regression through application of Barker's method, the quality of fit is considerably improved, as can be seen from plot C of Figure 4 and the statistics: root mean square $\Delta P = 0.77$ mm Hg and root mean square $\Delta y = 0.007$. The five-fold reduction in the root mean square ΔP resulting from use of Barker's method is most significant. It is evident from Figure 4C that Equation (6) is fully capable of reproducing the experimental P vs. x data to within the limits of experimental precision. However, when one incorporates the redundant measurements of y into the data-reduction process, the correlation is distorted to the extent that it no longer reproduces the measured P-x data. It is not the correlating equation that is at fault. Indeed, the experimental y values, whose measurement supposedly provides additional information and therefore a more reliable correlation, are markedly better reproduced by the correlation in which they are not used than by either of those in which they are. This may seem a surprising result, certainly one requiring explanation.

It was shown by Van Ness et al. (1973) that values of g/x_1x_2 and hence of g are very insensitive to errors in x and that errors in these quantities reflect primarily errors in P and y. Moreover, it was shown that correlations based on the full set of P-x-y data are virtually equivalent to correlations based just on P-y data. However, the fit is with respect to x, not y. Since experimental values of y are likely to be less reliable than those of x, the use of y values is likely to introduce errors that distort a correlation in which x is the independent variable. The effect, seen in Figures 4A and 4B is to introduce systematic deviations into the P-x relation and compensating deviations into the P-y relation, so that neither corresponds closely to the experimentally determined relationship. Barker's method, on the other hand, makes use of just the P-x data; if these are regarded as more reliable than the y values, this method produces the best fit of P consistent with the correlating equation employed. The excellence of the P vs. x fit is evident from Figure 4C. The minor bias of the Δy plot represents an indication of thermodynamic inconsistency in the P-x-y measurements (Van Ness et al., 1973). Though not serious here, it is this bias, caused by inconsistency, that distorts the correlation when g or g/x_1x_2 is fit. The problem does not lie with any deficiency of the correlating equation. When g or g/x_1x_2 is fit directly to x_1, the quality of fit is excellent, showing no systematic deviations or significant bias. However, when values of g are calculated from P-x-y data that are not perfectly consistent, then the equation which correlates these g's, when used for the recalculation of P's and y's, will not yield values in agreement with the experimental values, but rather will give a set of values which are thermodynamically consistent. If the redundant y values are in fact perfectly consistent with the P-x data, their use has no effect; if they are inconsistent, their use leads to self-

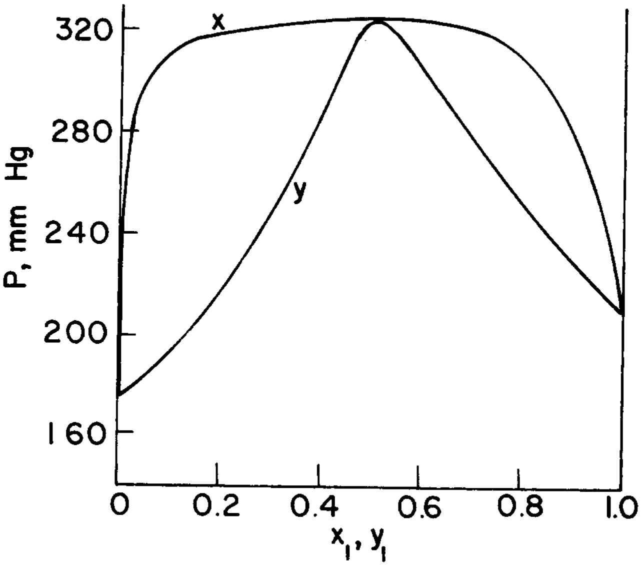

Fig. 5. *P-x-y* diagram for methanol(1)-carbon tetrachloride(2) at 35°C.

TABLE 2. PARAMETERS IN EQUATION (5) FOR CHLOROFORM(1)—ETHANOL(2) AT 35, 45, AND 55°C BY THREE FITTING PROCEDURES
Data of Scatchard and Raymond (1938)

Virial coefficients: 35°C: $B_{11} = -1200, B_{22} = -2320, B_{12} = -845$ cm³/mol
45°C: $B_{11} = -1085, B_{22} = -1870, B_{12} = -740$ cm³/mol
55°C: $B_{11} = -985, B_{22} = -1535, B_{12} = -655$ cm³/mol

	Fitting procedure, 35°C			Fitting procedure, 45°C			Fitting procedure, 55°C		
	g/x_1x_2 vs. x_1	g vs. x_1	P vs. x_1	g/x_1x_2 vs. x_1	g vs. x_1	P vs. x_1	g/x_1x_2 vs. x_1	g vs. x_1	P vs. x_1
A_{12}	0.3940	0.3102	0.3681	0.4854	0.4856	0.4611	0.5654	0.6061	0.5201
A_{21}	1.8393	1.7948	1.7960	1.6957	1.6969	1.7106	1.5766	1.5511	1.5767
λ_{12}	−0.4365	−0.8587	−0.5694	−0.3951	−0.3790	−0.4063	−0.4438	−0.1825	−0.4317
λ_{21}	1.0304	0.8161	0.8679	0.5444	0.5415	0.6935	0.6465	0.4553	0.5866
Root mean square ΔP	0.80	1.20	0.53	1.68	1.62	0.49	2.37	2.02	0.58
Root mean square Δy	0.0024	0.0036	0.0020	0.0040	0.0040	0.0029	0.0058	0.0052	0.0042

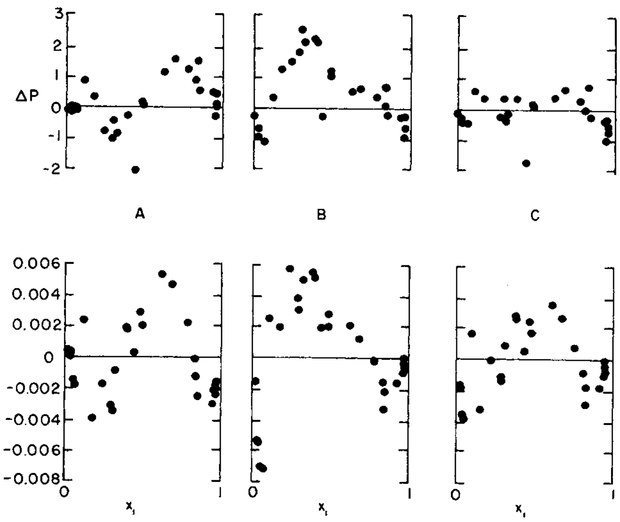

Fig. 6. ΔP(mm Hg) and Δy_1 vs. x_1 for chloroform(1)-ethanol(2) at 35°C: (A) based on fit of g/x_1x_2 vs. x_1, (B) based on fit of g vs. x_1, (C) based on fit of P vs. x_1. Data of Scatchard and Raymond (1938).

consistent but distorted P-x and y-x relations that exaggerate the deficiencies of the data. If one regards the x values or the P values as the least reliable, then data reduction should be based on the P-y or x-y data, and entirely different procedures are appropriate, as described by Van Ness et al. (1973) in Part I.

Plot D of Figure 4 compares P and y as calculated from Equation (6) and parameters determined from the P vs. x data of Scatchard et al. and Missen with the experimental data of Paraskevopoulos (1959), which were not used in any way in the development of the correlation. Although the root mean square ΔP is somewhat larger than that for the data on which the correlation is based, the root mean square Δy is less. Indeed, the agreement between calculated and experimental y's is remarkable.

In computing values of P and y from the correlation for comparison with a particular data set, we have in all cases used the values of P_1^{sat} and P_2^{sat} which go with that data set, not average values. The comparisons represented by Figures 4C and D indicate an excellent correlation of all data available for the methanol-carbon tetrachloride system at 35°C. Figure 5 shows the P-x-y diagram for this system. The extreme steepness of the P-x curve at low values of x_1 accounts for the great difficulty of taking data in this dilute region and in fitting them. The value of dP/dx_1 at values of x_1 near zero is about 5000 mm Hg. This means that errors in x_1 of ± 0.001 are equivalent to errors in P of ± 5 mm Hg. In view of this, it is worth noting that the values of x reported by Missen are given to just three figures.

The sets of data in the literature probably most often cited as representing a standard of quality are the P-x-y data of Scatchard and Raymond (1938) for chloroform-ethanol at 35°, 45°, and 55°C. This system has often been treated as a classical example of one fit by the 3-suffix Margules equation. As a matter of fact it conforms to Equation (5), the 5-suffix Margules equation. We have therefore correlated the data at each temperature by Equation (5) with each of the three procedures already described. The pure-component vapor pressures given by the authors cited have been used in all calculations. The results are summarized in Table 2. Again it is seen at all three temperatures that Barker's method produces a superior correlation. The quality of fit is very good indeed, best at 35°C and worst at 55°C. Figure 6 shows ΔP and Δy vs. x_1 for the data set at 35°C. Plots A and B, based on fits of g/x_1x_2 and g, though different in detail, are of equivalent quality. Plot C indicates the clear superiority of Barker's method. The deviations Δy of plot C give only the slightest indication of nonrandom behavior and hence of thermodynamic inconsistency. Nevertheless, the inconsistency is enough to distort the correlations when the y values are included in the data-reduction process, as is seen by comparison of Plots A and B with C.

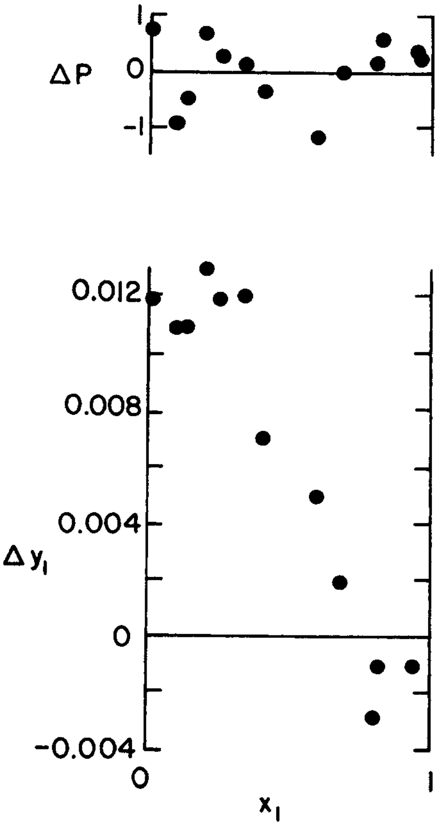

Fig 7. ΔP(mm Hg) and Δy_1 vs. x_1 for ethanol(1)-water(2) at 70°C. Data of Mertl (1972).

It is not difficult to find in the literature data sets which clearly do not meet the test of thermodynamic consistency. An example is the data set of Mertl (1972) for ethanol(1)-water(2) at 70°C. The P-x data are well correlated by Equation (6), the modified Margules equation with the following values for the parameters:

$$A_{12} = 1.8765 \qquad A_{21} = 0.9596$$
$$\alpha_{12} = 1.2810 \qquad \alpha_{21} = 0.4459$$
$$\eta = 0.0$$

The virial coefficients are

$$B_{11} = -1170 \text{ cm}^3/\text{mol}$$
$$B_{22} = -1105 \text{ cm}^3/\text{mol}$$
$$B_{12} = -\ 670 \text{ cm}^3/\text{mol}$$

Figure 7 shows the excellence of the correlation of the P-x values (root mean square $\Delta P = 0.56$ mm Hg); however, there is a clear bias to the Δy plot, indicating a definite departure from thermodynamic consistency. There is of course no way to be sure which of the experimental measurements are least reliable. However, if one concludes that the y's are most likely at fault, then one has measured these values only for the purpose of discarding them. If the correlation proceeds through g or g/x_1x_2, then the P-x relation is badly distorted, yielding root mean square ΔP's greater than 7 mm Hg.

Throughout these studies we have used standard numerical techniques and least-squares fitting procedures and

TABLE 3. RESULTS OF DATA REDUCTION FOR SIX BINARY SYSTEMS AT 50°C. PURE COMPONENT VAPOR PRESSURES, VIRIAL COEFFICIENTS, PARAMETERS FOR EQUATIONS (5) AND (6), AND PRESSURE DEVIATIONS

System	Acetone(1)—chloroform(2)	Acetone(1)—methanol(2)	Chloroform(1)—methanol(2)	Chloroform(1)—ethanol(2)	Chloroform(1)—*n*-heptane(2)	Ethanol(1)—*n*-heptane(2)
Type of Margules equation	4-suffix	3-suffix	5-suffix	5-suffix	4-suffix	Modified
P_1^{sat}, mm Hg	614.48	614.48	520.00	520.00	520.00	221.61
P_2^{sat}, mm Hg	520.00	417.18	417.18	221.61	141.92	141.92
B_{11}, cm³/mol	−1,425	−1,425	−1,030	−1,030	−1,030	−1,690
B_{22}, cm³/mol	−1,030	−1,200	−1,200	−1,690	−2,310	−2,310
B_{12}, cm³/mol	−785	−1,030	−595	−695	−1,300	−970
A_{12}	−0.8384	0.6523	0.8440	0.4713	0.3507	3.4301
A_{21}	−0.5685	0.6369	1.9208	1.6043	0.5262	2.4440
α_{12}	0.2182	—	—	—	0.1505	11.1950
α_{21}	0.2182	—	—	—	0.1505	2.3806
η	—	—	—	—	—	9.1369
λ_{12}	—	—	−0.0127	−0.3651	—	—
λ_{21}	—	—	0.6565	0.5855	—	—
Root mean square ΔP, mm Hg	0.75	0.70	0.30	0.56	0.54	0.34
Max $\|\Delta P\|$, mm Hg	2.36	1.92	0.54	1.01	0.90	0.60

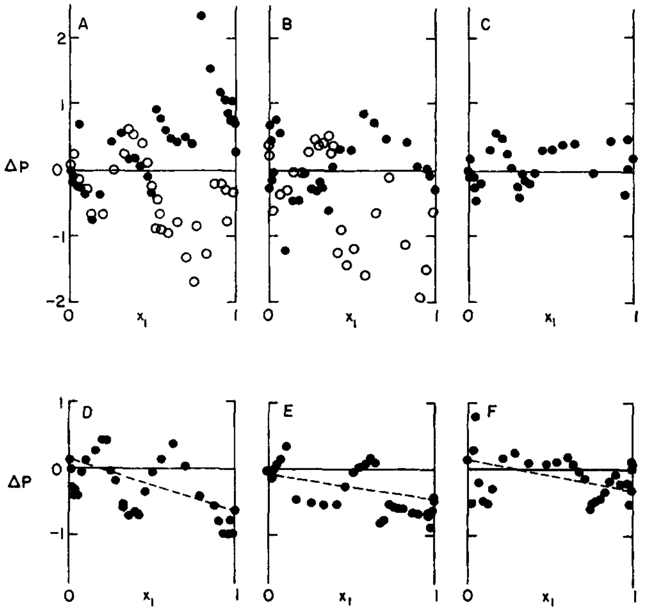

Fig. 8. ΔP(mm Hg) vs. x_1 for (A) acetone-chloroform [2 runs], (B) acetone-methanol [2 runs], (C) chloroform-methanol, (D) chloroform-ethanol, (E) chloroform-n-heptane, and (F) ethanol-n-heptane.

have encountered no convergence or lack-of-uniqueness problems in determination of the parameters for the correlating equations employed. Although other techniques and correlating equations might also be successfully applied, we have demonstrated a capability to correlate VLE data for highly nonideal systems, while at the same time providing a sensitive thermodynamic consistency test of the data. Our primary conclusion is that accurate measurement of *P-x* data assures reliable values of *y* through Barker's method of data reduction, provided the measured data are reproduced within the limits of experimental precision.

NEW DATA

Measurements of *P* vs. *x* have been made at 50°C by Floess (1973) and Walsh (1974) for the six binary systems: acetone-chloroform, acetone-methanol, chloroform-methanol, chloroform-ethanol, chloroform-*n*-heptane, and ethanol-*n*-heptane.* The experimental apparatus is described by Gibbs and Van Ness (1972). Data reduction was carried out by Barker's method applied to Equation (5) or (6) or to simpler Margules expressions representing special cases of these equations. All data points were weighted equally. The results are presented in Table 3.

Because the binary data reported here are part of a larger study of the ternary systems, acetone-chloroform-methanol and chloroform-ethanol-*n*-heptane, to be reported in Part IV of this series of papers, a single value for each P_i^{sat} has been established as the pure-component vapor pressure for each component for use in the entire data-reduction process. The values of P_i^{sat} listed in Table 3 are therefore averages of all pure-component vapor-pressure measurements taken during the course of this work whether made in connection with runs on binary or ternary mixtures. The range of measured values for any single component is less than 1 mm Hg and falls within the range of values reported in the literature. All measurements of solution vapor pressures for the binary systems reported here were corrected to these average P_i^{sat}'s according to Equation (16) prior to fitting. The comparison of calculated and experimental pressures for all systems is shown in Figure 8. The calculated values of *P* come from Equation (15) with g given by Equation (5) or (6) and with average values of the P_i^{sat}'s. The experimental values of *P* are the raw, uncorrected data. Therefore deviations in P_i^{sat} appear at $x_1 = 0$ and $x_1 = 1$ on these graphs, and the plot of ΔP may show slight bias, because the fit was made to corrected values of *P*. This is most clearly seen in plots D, E, and F of Figure 8. The ability of the equation to fit the data is best reflected by the bias on these plots with respect to the dashed lines, which connect the deviations in P_1^{sat} and P_2^{sat}. For the systems represented by plots A and B, two sets of data taken by two different operators are shown. The root mean square ΔP for each system is about 0.7 mm Hg, and this value is probably the one most indicative of the reliability of the *P-x* data.

Data are available in the literature for the acetone-chloroform system at 50°C (Mueller and Kearns, 1958; Röck and Schröder, 1957), for the acetone-methanol system at 55°C (Freshwater and Pike, 1967), and for

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* Tables of raw *P-x* data for all six systems have been deposited as Document No. 02523 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 2 Park Ave. So., New York 10016 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

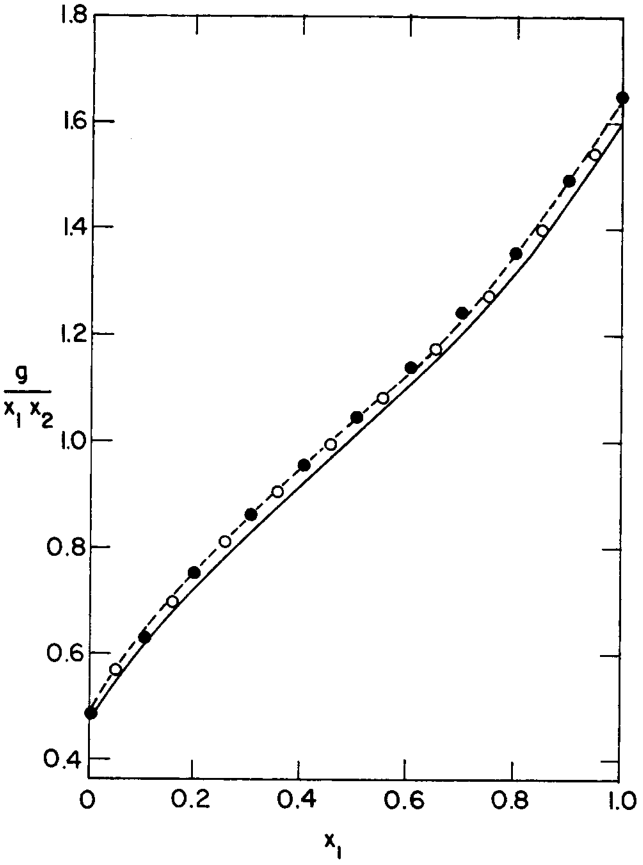

Fig. 9. g/x_1x_2 vs. x_1 for chloroform(1)-ethanol(2) at 50°C, showing the results of Scatchard and Raymond in comparison with those of the present work.

○ from 45°C data of Scatchard and Raymond (1938)
● from 55°C data of Scatchard and Raymond (1938)
— Present correlation, data of Walsh (1974)

methanol-chloroform at 49.3°C (Kireev and Sitnikov, 1941). All are in substantial agreement with our measurements. The results of Severns et al. (1955) will be discussed in Part IV in connection with the ternary system acetone-chloroform-methanol.

For a detailed comparison of our results with literature values, we return to the data of Scatchard and Raymond (1938) for the chloroform(1)-ethanol(2) system. These authors report comprehensive sets of data at both 45° and 55°C, the quality of which is indicated in Table 2. In order to treat their data on the same basis as our own, we fit their P-x data at both temperatures to Equation (5) by Barker's method. The resulting values of g for each temperature were corrected to 50°C according to the exact thermodynamic relation

$$\left(\frac{\partial g}{\partial T}\right)_x = -\frac{H^E}{RT^2}$$

through use of the heat-of-mixing data at 50°C of Shatas (1974). The resulting values are shown as points on Figure 9. They indicate very satisfactory consistency among the two sets of data and the heats of mixing. These points were then fit to Equation (5) to yield the final g/x_1x_2 vs. x_1 relation (dashed line of Figure 9) at 50°C based on Scatchard's data. Our own results, represented by Equation (5) with parameters as given in Table 3, appear as the solid line of Figure 9. The two curves on this very sensitive plot are seen to be almost exactly conformal. They differ by no more than 3% and lead to a root mean square difference in y values of about 0.003 with a maximum of 0.006. This agreement is remarkable considering that the two sets of measurements were made 35 years apart with chemicals of different origin and by two completely different experimental techniques.

Finally, we show in Figures 10 and 11 the g/x_1x_2 vs. x_1 relations provided by our correlations and the P-x-y plots that result from them. The wide variety of behavior exhibited by the systems studied is particularly to be noted.

ACKNOWLEDGMENT

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NOTATION

A_{12}, A_{21}, α_{12}, α_{21}, D, λ_{12}, λ_{21}, η = empirical parameters in Equations (5), (6), and (7)
B_{ij} = second virial coefficient
G^E = excess Gibbs function, liquid phase
g = G^E/RT
g(net), g (net) = functions defined by Equations (3) and (4)
H^E = excess enthalpy (heat of mixing), liquid phase
P = vapor pressure in general
P_i^{sat} = vapor pressure of pure i
R = universal gas constant
T = absolute temperature

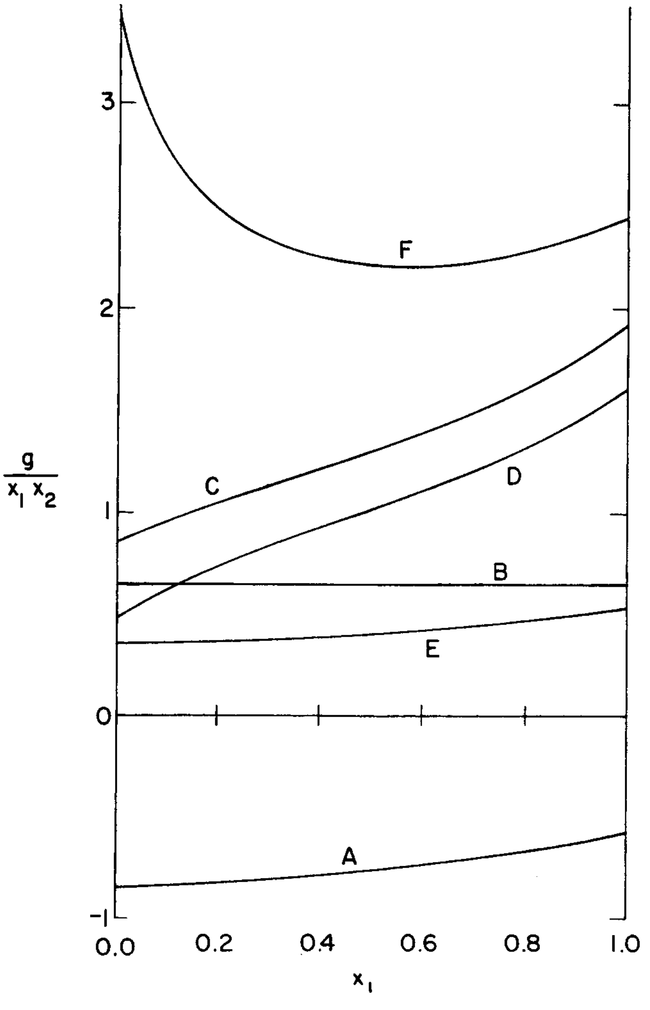

Fig. 10. g/x_1x_2 vs. x_1 at 50°C representing correlations for (A) acetone-chloroform, (B) acetone-methanol, (C) chloroform-methanol, (D) chloroform-ethanol, (E) chloroform-n-heptane, and (F) ethanol-n-heptane. First named compound is component 1

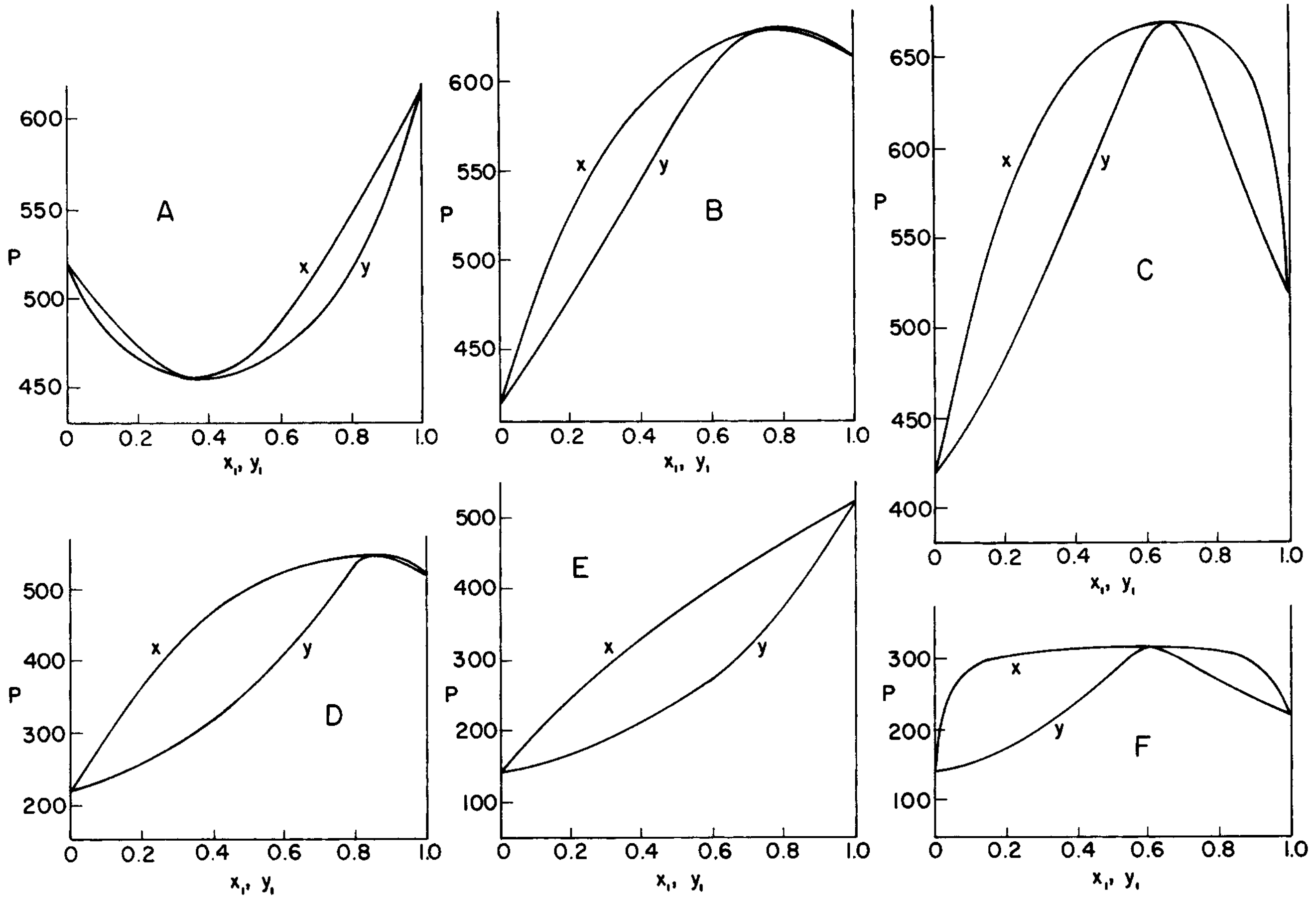

Fig. 11. *P*-x-y diagrams at 50°C for (A) acetone-chloroform, (B) acetone-methanol, (C) chloroform-methanol, (D) chloroform-ethanol, (E) chloroform-*n*-heptane, and (F) ethanol-*n*-heptane. First named compound is component 1. *P* is in mm Hg.

x = mole fraction, liquid phase
y = mole fraction, vapor phase

Greek Letters

γ_i = activity coefficient of component i, liquid phase
δ_{ij} = $2B_{ij} - B_{ii} - B_{jj}$
Φ_i = fugacity correction factor
ΔP, Δy = differences between calculated and experimental values
δP, δP_i^{sat} = corrections, related by Equation (16)
1, 2 = as subscripts, identify the two components of a binary system

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