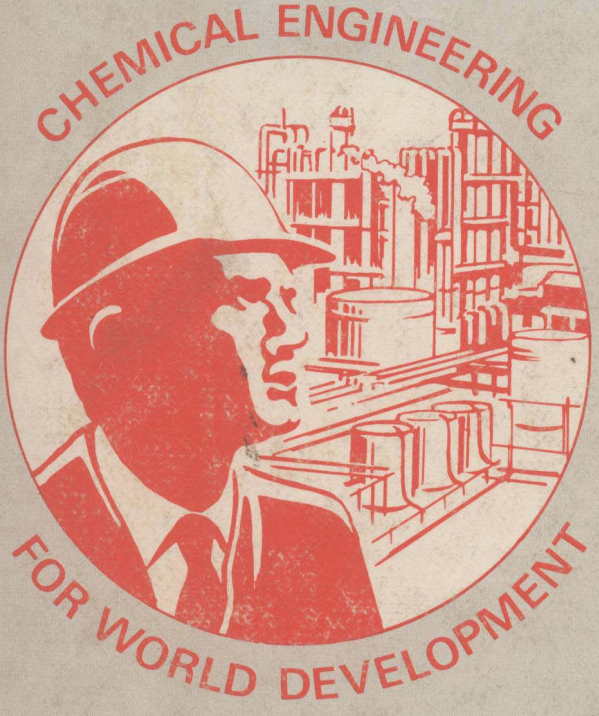

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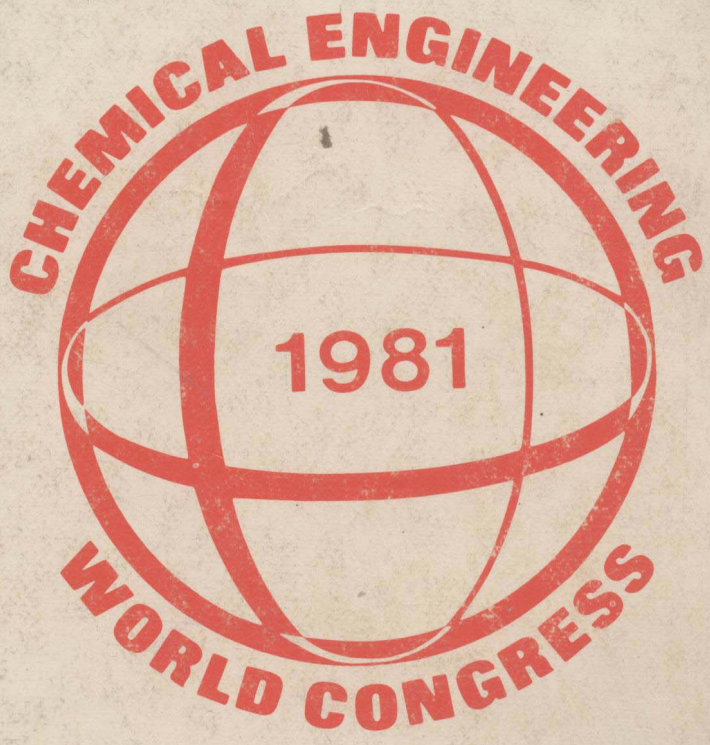

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- Fundamentals
- Control

Montréal, Canada 1981 October 4-9

IX Interamerican Congress of Chemical Engineering

31st Canadian Chemical Engineering Conference

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PREFACE

This volume contains the text of manuscripts received from authors prior to the printing deadline of July 27, 1981. The papers were printed directly from the best copy submitted. Since some of the manuscripts were not received by the Program Committee before the deadline, the Proceedings include only a partial collection of the presentations made at the 2nd World Congress of Chemical Engineering.

The Technical Program of the 2nd World Congress of Chemical Engineering and these Proceedings were the result of considerable effort by volunteers who do not appear on any list of committee members. We would like to thank the following students at McGill University for many hours of help: D. Abu-Fara, E. Chu, P. Higgins, A. Kallos, K. Kant, P. Lafleur, A. Menon, S. Sabade, M. Sahto and S. Soong. Secretarial services were cheerfully provided by Mrs. K. Brown and Mrs. K. Braginetz.

The Program Committee

VOLUME V

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SOME PRACTICAL CONSIDERATIONS IN REDUCTION OF VLE DATA

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For pressures below a few bars, vapor/liquid equilibrium (VLE) calculations require knowledge of activity coefficients γ_i for the liquid phase and of fugacity coefficients $\hat{\phi}_i$ for the vapor phase. The latter usually come from PVT data, but only VLE data themselves provide a basis for the correlation of activity coefficients. For example, the UNIFAC (Fredenslund et al., 1977) and ASOG (Kojima and Tochigi, 1979) group-contribution methods for activity coefficients, correlations of wide applicability, depend for validity on parameters evaluated from a large base of VLE data.

The essential property in VLE data reduction is the excess Gibbs function G^E of the liquid phase, and our primary objective is to find an equation that expresses the composition dependence of this function. In general, G^E depends not only on composition but on T and P as well. However, for the pressure range of interest, the influence of P is very small, and may safely be ignored. Restricting consideration to isothermal VLE data for binary systems, we therefore write

$$g^+ = g(x_1\,;\,\alpha,\beta,\ldots) \tag{1}$$

where $g \equiv G^E/RT$ and $\alpha, \beta, \ldots$ represent adjustable parameters. The superscript $^+$ indicates a value predicted from Eq. (1), and is affixed to all such quantities to distinguish them from corresponding values calculated directly from experimental data. Given Eq. (1) with specified values of the parameters, we can also determine predicted values of the activity coefficients:

$$\gamma_1^+ = \exp\left[g^+ + x_2\frac{dg^+}{dx_1}\right] \qquad (2a) \quad \text{and} \quad \gamma_2^+ = \exp\left[g^+ - x_1\frac{dg^+}{dx_1}\right] \qquad (2b)$$

For isothermal, binary VLE data, each experimental data point consists of the measured values x_1, P, and y_1. From these values for each point, one readily calculates experimental values of γ_1, γ_2, and g:

$$\gamma_i = \frac{y_i P \Phi_i}{x_i P_i^{sat}} \qquad (i = 1,2) \tag{3}$$

and

$$g = x_1 \ell n\gamma_1 + x_2 \ell n\gamma_2 \tag{4}$$

In Eq. (3) Φ_i is a factor of order unity that takes into account vapor-phase nonideality and the effect of pressure on the standard-state fugacity. We assume here that it can be properly evaluated. The traditional objective of data reduction has been to find values for the parameters α, β, ... in Eq. (1) that yield predicted values of γ_1^+, γ_2^+, or g^+ in close agreement with the experimental values of γ_1, γ_2, or g. The procedure is best implemented through residuals,

$$\delta\gamma_1 \equiv \gamma_1^+ - \gamma_1\,;\quad \delta\gamma_2 \equiv \gamma_2^+ - \gamma_2\,;\quad \delta g \equiv g^+ - g$$

and minimization of a sum

$$S \equiv \sum (\delta Y)^2$$

where δY represents one of the residuals or perhaps some combination of them. This sum is called an objective function, and the process of minimization is known as regression. Highly efficient computer programs are available for carrying out the process. They simply take given starting values for the parameters α, β, ... and adjust them in a rational and systematic way until values are found that minimize S.

If Eq. (1) is of the proper form, then the residuals that remain after minimization scatter about zero; otherwise the residuals are biased from zero, and the process must be repeated with alternative equations until the fit is judged satisfactory. Examples of possible correlating equations are those of van Laar, Margules, and Wilson.

Experience shows that reduction of a given data set by minimization of different objective functions almost always yields alternative sets of values for the parameters α, β, ... With a proper correlating equation, all of the traditional methods yield final residuals that scatter about zero. Thus, one cannot judge the relative merits of these data-reduction procedures by how well they achieve agreement between predicted and experimental values of the thermodynamic functions on which they are based. The only proper basis for comparison is how well the different correlating equations reproduce the experimental values of the dependent variables P and y_1.

Associated with each predicted value of an activity coefficient γ_i^+, as given by Eqs. (2), are the corresponding predicted values P^+ and y_i^+; the relation is analogous to Eq. (3):

$$\gamma_i^+ = \frac{y_i^+ P^+ \Phi_i}{x_i P_i^{sat}} \qquad (i = 1,2) \tag{5}$$

Solving this equation for $y_i^+P^+$ and writing it for each species gives

$$y_1^+P^+ = \frac{x_1\gamma_1^+P_1^{sat}}{\Phi_1} \qquad (6a) \quad \text{and} \quad y_2^+P^+ = \frac{x_2\gamma_2^+P_2^{sat}}{\Phi_2} \qquad (6b)$$

By addition,

$$P^+ = \frac{x_1\gamma_1^+P_1^{sat}}{\Phi_1} + \frac{x_2\gamma_2^+P_2^{sat}}{\Phi_2} \tag{7}$$

and by Eq. (6a)

$$y_1^+ = \frac{x_1\gamma_1^+P_1^{sat}}{P^+\Phi_1} \tag{8}$$

For fixed T and a given value of x_1, these equations allow calculation of predicted values P^+ and y_1^+ from any correlating expression for g^+. When calculated at the experimental values of x_1 (with P_i^{sat} determined by T), they may be combined with the experimental values P and y_1 to form the residuals

$$\delta P \equiv P^+ - P \quad \text{and} \quad \delta y_1 \equiv y_1^+ - y_1$$

Indeed, these are the primary residuals, because they make direct comparisons between predicted values and actual experimental measurements, and they demonstrate directly the effectiveness of any data-reduction procedure in reproducing experimental values of the dependent variables P and y_1.

Data reduction can perfectly well be based on objective functions formed from the primary residuals themselves. We can, for example, find the values of α, β, ... which minimize

$$S \equiv \sum (\delta P)^2$$

This procedure was first proposed by Barker (1953), and is known as Barker's method. Its most striking feature is that the measured y_1 values play no part in the data-reduction process. Strictly, the secondary quantities Φ_i in Eqs. (7) and (8) should be written Φ_i^+. Thus, they actually depend on P^+ and y_1^+, initial values of which come from Eqs. (7) and (8) with $\Phi_i^+ = 1$. Simple iteration leads to final values of Φ_i^+,

P^+, and y_1^+. Measured values of P and y_1 are needed only for evaluation of the residuals δP and δy_1. Experience shows that one can always find a correlating equation by this procedure which produces final δP residuals that scatter about zero. When the δy_1 residuals from the same equation also scatter about zero, the data are said to be consistent, because the predicted y_1^+ values, which depend only on the x_1, P data, are in essential agreement with the measured y_1 values. However, the δy_1 residuals often show systematic deviations from zero. In this event, the data are inconsistent, and reflect systematic error somewhere in the data set. Here, the influence of all systematic error, whatever its source, appears in the δy_1 residuals.

An alternative to Barker's method again calculates P^+ and y_1^+ by Eqs. (7) and (8), but minimizes the objective function

$$S \equiv \sum (\delta y_1)^2$$

This procedure makes no use of the measured values of P, and is in principle the converse of Barker's method. However, experience shows in many cases that no correlating equation can be found that yields final δy_1 residuals that scatter about zero. The best possible fit then results in δy_1 residuals that are biased from zero. The reason lies in a thermodynamic relationship which constrains these residuals. Division of Eq. (5) by Eq. (3) gives

$$\frac{\gamma_i^+}{\gamma_i} = \frac{y_i^+ P^+}{y_i P}$$

If we divide this equation written for i = 1 by the same equation written for i = 2, the result is

$$\frac{\gamma_1^+/\gamma_2^+}{\gamma_1/\gamma_2} = \frac{y_1^+/y_2^+}{y_1/y_2}$$

We express this in logarithmic form as

$$\ell n \frac{\gamma_1^+}{\gamma_2^+} - \ell n \frac{\gamma_1}{\gamma_2} = \ell n y_1^+ - \ell n y_1 - (\ell n y_2^+ - \ell n y_2) = \delta \ell n y_1 - \delta \ell n y_2$$

or

$$\frac{\delta y_1}{y_1} - \frac{\delta y_2}{y_2} = \ell n \frac{\gamma_1^+}{\gamma_2^+} - \ell n \frac{\gamma_1}{\gamma_2}$$

Since $y_1 + y_2 = 1$ and $\delta y_2 = -\delta y_1$, this becomes

$$\frac{\delta y_1}{y_1 y_2} = \ell n \frac{\gamma_1^+}{\gamma_2^+} - \ell n \frac{\gamma_1}{\gamma_2}$$

Multiplying by dx_1 and integrating from $x_1 = 0$ to $x_1 = 1$, we get

$$\int_0^1 \frac{\delta y_1}{y_1 y_2} dx_1 = \int_0^1 \ell n \frac{\gamma_1^+}{\gamma_2^+} dx_1 - \int_0^1 \ell n \frac{\gamma_1}{\gamma_2} dx_1 \qquad (9)$$

The first integral on the right is necessarily zero; this follows from Eqs. (2a) and (2b). Writing these equations in logarithmic form and subtracting, we get

$$\ell n \gamma_1^+ - \ell n \gamma_2^+ = (x_1 + x_2) \frac{dg^+}{dx_1}$$

or

$$dg^+ = \ell n \frac{\gamma_1^+}{\gamma_2^+} dx_1$$

Integration from $x_1 = 0$ to $x_1 = 1$ gives

$$g^+(x_1 = 1) - g^+(x_1 = 0) = \int_0^1 \ell n \frac{\gamma_1^+}{\gamma_2^+} dx_1 = 0 \qquad (10)$$

because $g^+(x_1 = 1) = g^+(x_1 = 0) = 0$. Equation (9) therefore becomes

$$\int_0^1 \frac{\delta y_1}{y_1 y_2} dx_1 = - \int_0^1 \ell n \frac{\gamma_1}{\gamma_2} dx_1 \qquad (11)$$

The Gibbs-Duhem equation is implicit in Eqs. (2a) and (2b) and hence in Eq. (10). This is not the case for the integral on the right of Eq. (11), which depends solely on the experimental data, independent of the correlating equation. If the experimental activity coefficients do satisfy the Gibbs-Duhem equation, the data are consistent, and the integrals of Eq. (11) are also zero. If the experimental activity coefficients do not satisfy the Gibbs-Duhem equation the data are inconsistent. However the integrals of Eq. (11) may still be zero, because a zero value is only a necessary and not a sufficient condition for consistency of the data. When these integrals are zero, one can always find a correlating equation by minimization of $\sum(\delta y_1)^2$ that produces final residuals δy_1 that scatter about zero. When the δP residuals from the same correlation also scatter about zero, the data are consistent; when they do not, the data are inconsistent. When the integrals of Eq. (11) are not zero, as is often (but not necessarily) the case for inconsistent data, the δy_1 residuals cannot scatter about zero, and the best one can achieve by minimization of $\sum(\delta y_1)^2$ is a set of final δy_1 residuals that scatter about a mean value rather than about zero. No correlating equation exists that can yield a set of δy_1 residuals with smaller bias from zero. A complete assessment of the inconsistency of the data of course requires examination of the δP residuals along with the δy_1 residuals.

The vast majority of VLE data sets exhibit inconsistency to some degree. In this event, no correlating equation exists that produces sets of δP and δy_1 residuals that both scatter about zero. By minimizing either $\sum(\delta P)^2$ or $\sum(\delta y_1)^2$ through Eqs. (7) and (8), one finds correlating equations which yield on the one hand the best possible fit to the P, x_1 data and on the other hand the best possible fit to the y_1, x_1 data. These represent the proper extremes of data-reduction procedures. If there is reason to trust one part of the data set rather than the other, then a choice of one extreme or the other is indicated. However, a more appropriate choice is often a compromise fit wherein the effect of inconsistency in the data is apportioned between the δP and δy_1 residuals. This is accomplished by definition of a composite objective function

$$S \equiv \sum \left(\frac{\delta P}{w_P}\right)^2 + \sum \left(\frac{\delta y_1}{w_y}\right)^2 \qquad (12)$$

where w_P and w_y are normalizing factors which make the residuals compatible for simultaneous treatment. Suitable normalizing factors obtain when w_P is taken as the root-mean-square value of δP resulting from minimization of $\sum(\delta y_1)^2$ and w_y is taken as the root-mean square value of δy_1 resulting from minimization of $\sum(\delta P)^2$. However, these values may be adjusted so as to weight the residuals in any reasonable way.

Residuals in the thermodynamic functions are directly related to the primary residuals δP and δy_1. These relationships derive from Eq. (3), written here, for simplicity, without the secondary function Φ_i:

$$\gamma_i \simeq \frac{y_i P}{x_i P_i^{sat}} \qquad (i = 1,2) \tag{13}$$

For given values of x_i and P_i^{sat}, differentiation yields

$$\delta\gamma_i \simeq \frac{y_i}{x_i P_i^{sat}}\,\delta P + \frac{P}{x_i P_i^{sat}}\,\delta y_i$$

With Eq. (13), this becomes

$$\delta\gamma_i \simeq \gamma_i\left(\frac{\delta P}{P} + \frac{\delta y_i}{y_i}\right)$$

Thus, for species 1 and 2,

$$\delta\gamma_1 \simeq \gamma_1\left(\frac{\delta P}{P} + \frac{\delta y_1}{y_1}\right) \tag{14}$$

and

$$\delta\gamma_2 \simeq \gamma_2\left(\frac{\delta P}{P} - \frac{\delta y_1}{y_2}\right) \tag{15}$$

Differentiation of Eq. (4) for given values of x_1 and x_2 yields

$$\delta g = x_1\,\delta \ln\gamma_1 + x_2\,\delta \ln\gamma_2 = x_1\frac{\delta\gamma_1}{\gamma_1} + x_2\frac{\delta\gamma_2}{\gamma_2}$$

With Eqs. (14) and (15), this becomes, upon simplification,

$$\delta g \simeq \frac{\delta P}{P} + (x_1 - y_1)\frac{\delta y_1}{y_1 y_2} \tag{16}$$

Data reduction may be based on minimization of an objective function formed from any of the residuals $\delta\gamma_1$, $\delta\gamma_2$, or δg of Eqs. (14), (15), or (16). Experience shows that one can always find a correlating equation which produces final values of the $\delta\gamma_1$, $\delta\gamma_2$, or δg residuals that scatter about zero. This result is consistent with δP and δy_1 residuals that both also scatter about zero, as should be the case for strictly consistent data. However, with inconsistent data, the δP and δy_1 residuals cannot both scatter about zero, and the final $\delta\gamma_1$, $\delta\gamma_2$, or δg residuals must be combinations of offsetting δP and δy_1 residuals in accord with Eqs. (14), (15), or (16). In Eq. (14), these residuals combine by addition, producing a trend to opposite signs in the values of δP and δy_1. In Eq. (15), they combine by difference, and the trend is to like signs in the values of δP and δy_1. In Eq. (16), the trend depends on the sign of $(x_1 - y_1)$; this of course changes at an azeotrope. Data-reduction procedures based on the $\delta\gamma_1$, $\delta\gamma_2$, and δg residuals often do not yield sets of δP and δy_1 residuals that are compromises between the best fits of these residuals. These procedures are not constrained simply to apportion the effects of data inconsistencies between the δP and δy_1 residuals. Rather, they are free to generate inflated values of δP and δy_1 which offset each other in the minimization process. This applies to all data-reduction procedures based on residuals in thermodynamic functions or on combinations of such residuals. Every advantage lies with direct treatment of the primary residuals δP and δy_1.

We show the results of four different data-reduction procedures with a set of VLE data for chloroform(1)/ethanol(2) at 45°C (Scatchard and Raymond, 1938) which has always been considered of high quality. The general character of the data (25 x_1, P, y_1 points) is shown by Figure 1. The only notable feature is an azeotrope at a mole fraction of about 0.88. The four-parameter Margules equation is suitable for correlation of the data:

$$\frac{g^+}{x_1 x_2} = A_{21}x_1 + A_{12}x_2 - (C_{21}x_1 + C_{12}x_2)x_1 x_2$$

Data reduction yields values for the parameters A_{21}, A_{12}, C_{12}, and C_{21}. Figure 2 shows the final residuals δP and δy_1 which result when the objective function is $\sum(\delta P)^2$. Clearly the δP residuals scatter about zero, showing the suitability of form of the correlating equation. However, the δy_1 residuals do not scatter about zero, showing that the data are in some degree inconsistent.

When the objective function is $\sum(\delta y_1)^2$, the results are those shown by Figure 3. Neither the δP nor δy_1 residuals scatter about zero. The δy_1 residuals fail to do so because of the constraint imposed by Eq. (11). However, this is the best possible fit of the y_1 data.

Figure 4 shows the results of a compromise fit based on the objective function of Eq. (12) with normalizing factors determined as described in discussion of Eq. (12).

Finally, Figure 5 shows the δP and δy_1 residuals that result from minimization of $\sum(\delta g)^2$. The quantity $(x_1 - y_1)$ in Eq. (16) is here negative at all values of x_1 up to the azeotrope at $x_1 = 0.88$. Thus, over most of the composition range the δP and δy_1 residuals combine by difference, and can offset each other only if they have the same sign. This trend is clear in Figure 5. However, for x_1 values above 0.8, the difference $(x_1 - y_1)$ is very small, and the second term of Eq. (16) makes but a small contribution. The fit then tends to minimize the δP residuals, which in this region are seen to be very small.

A quantitative indication of the quality of these various results is given by Table 1, which lists the root-mean-square values of δP and δy_1 for all four fitting procedures. Clearly, minimization of $\sum(\delta P)^2$ produces the lowest value of RMS δP, and minimization of $\sum(\delta y_1)^2$ yields the lowest value of RMS δy_1. Minimization of the residual defined by Eq. (12) obviously yields a true compromise fit, with RMS δP and δy_1 values falling between those obtained by separate minimization of $\sum(\delta P)^2$ and $\sum(\delta y_1)^2$. By comparison, minimization of $\sum(\delta g)^2$ does poorly, yielding the largest RMS δy_1 of any procedure.

The minimization of $\sum(\delta g)^2$ is particularly direct and uncomplicated, and was widely implemented by hand calculation long before the advent of computers. In fact, it became firmly established as the standard procedure of VLE data reduction, both in the minds of thermodynamicists and in their textbooks. A long-standing practice is not easily displaced, but with the ready availability of computers there is every reason to abandon an outmoded procedure in favor of one that produces better results.

We have not considered in this paper the statistical techniques that might be incorporated into data-reduction procedures. A pre-condition to application of these methods is a data set free of systematic error, at the very least, a set of consistent data. For the rare set of data that satisfies this condition, statistical methods effectively solve the relatively minor problem of how best to fit data that are correct to within random error.

Although we have considered here only the case of isothermal data, the same general procedures apply to the constant-pressure case, as discussed by Van Ness and Abbott (1981).

Literature Cited

Barker, J.A., "Determination of Activity Coefficients from Total Pressure Measurements," Austral. J. Chem., 6, 207-210, 1953.

Fredenslund, A., J. Gmehling, and P. Rasmussen, Vapor-Liquid Equilibria Using UNIFAC, Elsevier, Amsterdam, 1977.

Kojima, K. and T. Tochigi, Prediction of Vapor-Liquid Equilibria by the ASOG Method, Elsevier, Amsterdam, 1979.

Scatchard, G. and C.L. Raymond, "Vapor-Liquid Equilibrium. II. Chloroform-Ethanol Mixtures at 35, 45, and 55°C," J. Am. Chem. Soc., 60, 1278-1287, 1938.

Van Ness, H.C. and M.M. Abbott, Classical Thermodynamics of Nonelectrolyte Solutions with Applications to Phase Equilibria, McGraw-Hill, New York, 1981.

Table 1. Root-Mean-Square Values of δP and δy_1 for Different Data-Reduction Procedures. Ethanol(1)/Chloroform(2) at 45°C.

S	RMS δP	RMS δy_1
$\sum(\delta P)^2$	0.07	0.0030
$\sum(\delta y_1)^2$	0.33	0.0017
Eq. (12)	0.15	0.0022
$\sum(\delta g)^2$	0.22	0.0043

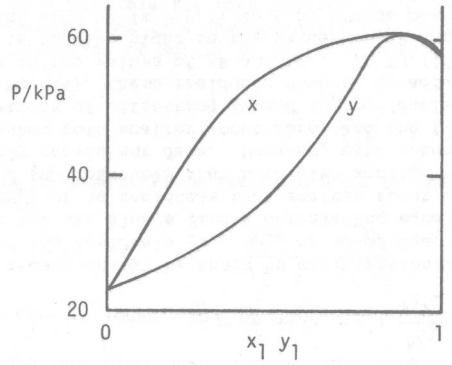

Figure 1. VLE data for chloroform(1)/ethanol(2) at 45°C.

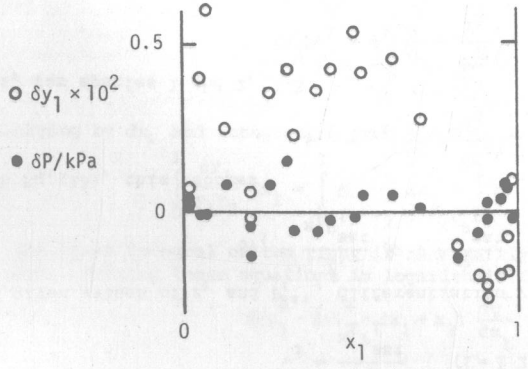

Figure 2. Residuals from fit based on minimization of $\sum(\delta P)^2$.

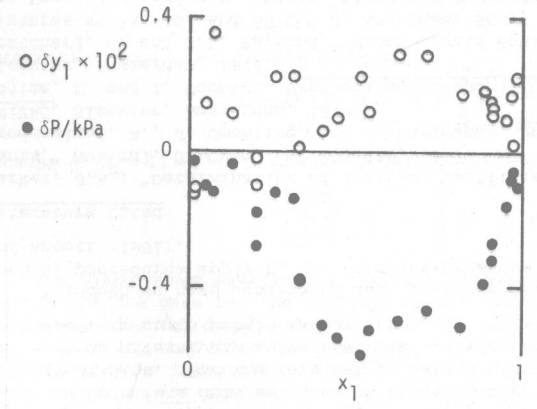

Figure 3. Residuals from fit based on minimization of $\sum(\delta y_1)^2$.

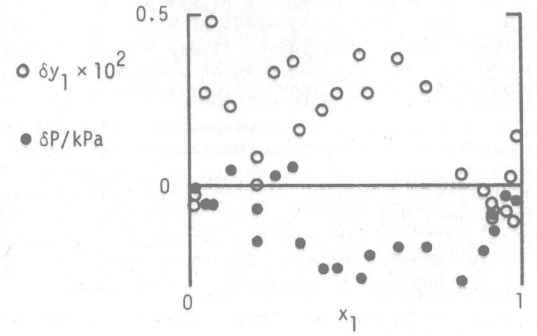

Figure 4. Residuals from fit based on minimization of the objective function given by Eq. (12).

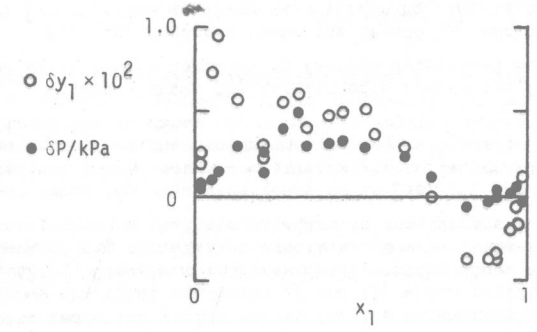

Figure 5. Residuals from fit based on minimization of $\sum(\delta g)^2$.