Jameson, G. J., "Some operating characteristics of the resonant bubble contactor," *Trans. Instn. Chem. Engrs.*, 44, T91 (1966).

Johnson, D. L., H. Saito, J. D. Polejes, and O. A. Hougen, "Effect of bubbling and stirring on mass transfer coefficients in liquids," *AIChE J.*, 3, 411 (1957).

Lemcoff, N. O., "Mass transfer and hydrogenation of acetone in a vibrating slurry reactor," Ph.D. thesis, Univ. London (1974).

———., and G. J. Jameson, "Solid-liquid mass transfer in a resonant bubble contractor," *Chem. Eng. Sci.*, 30, 363 (1975).

Petersen, E. E., *Chemical Reaction Analysis*, Chap. 4, Prentice-Hall, Englewood Cliffs, N. J. (1965).

Price, R. H., and D. B. Schiewetz, "Catalytic liquid phase hydrogenation," *Ind. Eng. Chem.*, 49, 807 (1957).

Satterfield, C. N., *Mass transfer in heterogeneous catalysis*, Chaps. 1-3, MIT Press, Cambridge, Mass. (1970).

Sherwood, T. K., and E. J. Farkas, "Studies of the slurry reactor," *Chem. Eng. Sci.*, 21, 573 (1966).

Snyder, J. R., P. F. Hagerty, and M. C. Malstad, "Operation and performance of bench scale reactors," *Ind. Eng. Chem.*, 49, 689 (1957).

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Method of Evaluation and Reduction of Vapor-Liquid Equilibrium Data of Binary Mixtures

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A new method to reduce vapor-liquid equilibrium data of binary mixtures and to evaluate a thermodynamic model is presented. It is based on the principle of maximum likelihood. Deviations between all measured and predicted quantities are calculated and confidence limits in model parameters are evaluated from the given estimates of experimental errors. Many examples illustrate the practical applications of the method.

SCOPE

The purpose of this work is to introduce new concepts in the mathematical treatment of experimental data of vapor-liquid equilibria of binary mixtures. There has been a great emphasis in the literature on consistency tests and comparison of thermodynamic models for the representation of these data. In view of the application of vapor-liquid equilibria to the design of industrial distillations, molecular theories do not provide a predictive method which could be tested only with a few data. One should instead rely on semi-empirical models with adjustable parameters. From classical thermodynamics, we know that such model can be formulated as an expression of the excess Gibbs energy as a function of composition and temperature. Unknown parameters in this function are adjusted upon experimental data. Usual methods of reduction of data yield the optimal values of the parameters only. But much more can be obtained from a careful application to the physical problem of the methods of applied statistics. In this perspective, one should consider as result of experimental measurement not only the value of a variable but also the standard deviation which can be estimated from reproducibility tests. Besides the optimal values of the parameters, the present mathematical treatment gives many other results, from which one can draw conclusions about both the validity of data and suitability of the excess Gibbs energy equation. The results are also useful in planning experiments for a specific utilization.

CONCLUSIONS AND SIGNIFICANCE

In this paper, a new method of treatment of experimental vapor-liquid data of binary mixtures is presented. It is based on the principle of maximum likelihood. A gaussian distribution of random error is assumed for all experimental measurements and an estimate of its variance is used as input to the calculation. The results of the treatment are:

1. Values of the parameters in a given expression for excess Gibbs energy, for instance, those of Van Laar or the NRTL model.
2. Estimate of the error in the values of the parameters.
3. Individual deviation between calculated and experimental value of each measured variables.

It is shown that this method of treatment of data is advantageous to check the validity of experimental measurement, compare models for vapor-liquid equilibria, evaluate their flexibility, verify the independence of parameters, and assess the necessary experimental information for the prediction of vapor-liquid data in an industrial problem of separation.

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Vapor-liquid equilibrium data are very numerous (Wichterle et al., 1973) in the literature but not of equivalent merit, and their value is difficult to assess by the user.

Evaluation of experimental data has been made traditionally by tests of consistency. However, recent papers have questioned the former use of the area test; Van Ness et al. (1973) recommend concentration of efforts in improving measurements rather than obtaining redundant data for such tests; Samuels et al. (1972) and Ulrichson and Stevenson (1972) redirect the attention towards the effect of random errors, incorporating the experimental evaluation of these errors into the use of a test.

The problem of data reduction can be solved simultaneously with data evaluation. Data reduction is a transformation of the information given by individual experimental measurements into a condensed form suitable for further use in phase equilibrium calculations. This paper proposes a method of conducting simultaneously the evaluation of complete binary vapor-liquid data when the composition of vapor and liquid are measured, along with pressure and temperature, and their reduction by a thermodynamic model. A thermodynamic model is an expression of the excess Gibbs energy $g^E(x_1, T, \mathbf{C})$.

The NRTL model described by Renon and Prausnitz (1968) has been chosen for the semi-empirical expression of the excess Gibbs energy:

$$g^E = RT\, x_1 x_2 \left[\frac{\tau_{21} \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} + \frac{\tau_{12} \exp(-\alpha_{12}\tau_{12})}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \right] \quad (1)$$

where

$$\tau_{jk} = \frac{C_{jk}}{RT} = \frac{1}{RT}(\epsilon_{jk} - \epsilon_{jj}) \quad (2)$$

This equation contains three adjustable parameters (C_{21}, C_{12}, α_{12}). Activity coefficients are derived from Equation (1) by classical differentiation (Prausnitz, 1969). The method of reduction is not restricted to this particular model.

PRINCIPLE OF MAXIMUM LIKELIHOOD

The values of the parameters of the model are chosen to minimize the deviations between activity coefficients calculated from experimental data by the following equation:

$$\gamma_l^{\text{exp.}} = \frac{y_l\, \phi_l\, P}{x_l\, f_l^{0L*}\, N_l} \qquad l = 1, 2 \quad (3)$$

and their values derived from the model $\gamma_l^{\text{caltd}}(x_1, T, \mathbf{C})$. The vapor phase fugacity coefficients can generally be predicted for low pressure data considered here (O'Connel and Prausnitz, 1967; Nothnagel et al., 1973; Tsonopoulos, 1974).

Very often the least square technique is used, which minimizes a weighted sum of squared residuals. The residual r_{li} is defined by the following relation:

$$r_{li} = \gamma_{li}^{\text{exp}}(x_{1i}, y_{1i}, P_i, T_i) - \gamma_{li}^{\text{caltd}}(x_{1i}, T_i, \mathbf{C}) \qquad l = 1, 2 \quad (4)$$

where subscript i refers to experiment i and $\mathbf{C}$ to the parameters of the model in vector notation. The weighting factors give more or less importance to each experiment in the reduction.

A more rigorous approach is the application of the principle of maximum likelihood as described by Bard and Lapidus (1968). It maximizes the probability that all residuals r_{li} are equal to their estimated errors with the two following assumptions:

1. Errors on experimental values of activity coefficients in different experiments (different i) are independent.
2. These errors have a gaussian distribution.

When all the uncertainties in the observed variables (x_{1i}, y_{1i}, P_i, T_i) are known for each experiment i, it can be shown that this principle leads to the minimization of S defined as

$$S = \sum_{i=1}^{n} \mathbf{r}_i^t\, \mathcal{VAR}^{-1}(\mathbf{r}_i)\, \mathbf{r}_i \quad (5)$$

In this expression $\mathbf{r}_i$ is the vector (r_{1i}, r_{2i}) and $\mathcal{VAR}(\mathbf{r}_i)$ a symmetrical matrix called the *variance covariance matrix*, the terms of which are

1. Diagonal terms $l - l$ equal to the error variance in the residual r_{li} which is the mean value of the quantity $[(\delta r_{li})_\mu]^2$ when a large number of measurements (expressed here by subscript μ) is made for the same experiment i.
2. Off diagonal terms equal to the mean value of the quantity $(\delta r_{1i})_\mu\,(\delta r_{2i})_\mu$. This term is the covariance between the two errors in residuals. Estimates of variances $\sigma^2(r_{li})$ and covariances $\text{cov}(r_{1i}, r_{2i})$ are obtained from the uncertainties in each measured variable z_{ji} (respectively, x_{1i}, y_{1i}, P_i, T_i for $j = 1, \ldots, 4$) using the following equations:

$$\sigma^2(r_{li}) = \sum_{j=1}^{4} (\partial r_l/\partial z_j)_i^2\, \sigma_i^2(z_j) \quad (6)$$

$$\text{cov}(r_{1i}, r_{2i}) = \sum_{j=1}^{4} (\partial r_1/\partial z_j)_i\, (\partial r_2/\partial z_j)_i\, \sigma_i^2(z_j) \quad (7)$$

The experimental uncertainties on measured variables are deduced from reproducibility tests and assumed to be equal to the standard deviations of the experimental random errors, which are gaussian with zero mean value. These uncertainties, which may vary from one experiment to another, are of great importance in this method and their choice should be made with great care when using literature data.

The minimum of S with respect to vector $\mathbf{C}$ is found by the classical Gauss-Newton procedure. All partial derivatives $\partial S/\partial C_k$ are zero for $k = 1, \ldots, m$ after linearization. It leads to the following matrix equation to compute $\boldsymbol{\Delta}\mathbf{C}$:

$$\mathcal{A} \cdot \boldsymbol{\Delta}\mathbf{C} = \mathbf{B} \quad (8)$$

(Details of calculation are given in Appendix A.)

The principle of maximum likelihood as applied here gives another element of great importance in data reduction. It can be shown (Appendix A) that in the last iteration steps the matrix $\mathcal{A}^{-1}$ is a good estimate of the variance covariance matrix $\mathcal{VAR}(\mathbf{C})$ of the parameters. The terms of this matrix were defined earlier and confidence limits in the parameters are proportional to them. This result was also shown by Péneloux and Deyrieux (1973).

PREDICTED VALUES OF MEASURED VARIABLES

Usually (Renon et al., 1972; Prausnitz et al., 1967) the vapor-liquid data predicted by the thermodynamic model are calculated by choosing two independent variables (T, x_1) giving them their measured values and calculating the two others (P, y_1) by solving Equations (3), where γ_l^{exp} is replaced by γ_l^{caltd} the activity coefficients predicted by the model using the values of parameters previously obtained. Our present method takes into account the estimated experimental errors and calculates values of all measured quantities.

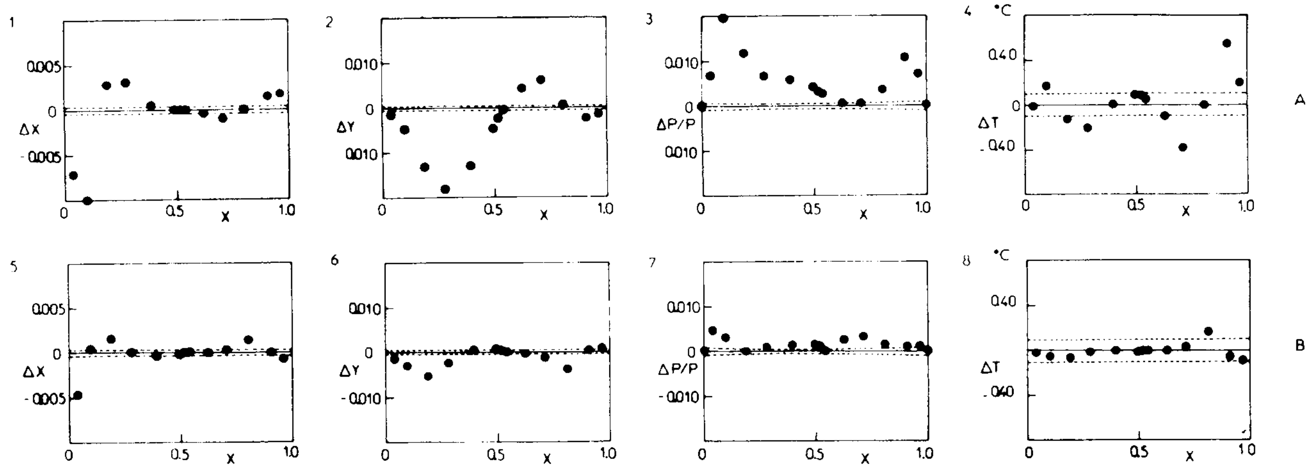

Fig. 1. Acetonitrile (1)—CCL$_4$ (2). A—reduction with $\alpha_{12} = 0.20$; B—three adjusted parameters.

A distance d is defined between experimental and calculated points by

$$d^2 = \sum_{j=1}^{4} \frac{(z_j^{\text{exp}} - z_j^{\text{caltd}})^2}{\nu(z_j)^2} \tag{10}$$

where $\nu(z_j)^2$ is proportional to the variance $\sigma^2(z_j)$ of experimental measurement of variable z_j. The z_j^{caltd}'s are obtained by minimizing d^2 with two constraints due to equilibrium equations. Lagrange's multipliers are used to take these constraints into account.

The present method is similar to the procedure developed independently by Abrams (1974), which differs in the calculation of the predicted points.

ANALYSIS OF INDIVIDUAL DEVIATIONS

The deviations between measured quantities z_j^{exp} (that is, x_1, y_1, P, T) and their calculated values z_j^{caltd} are very useful to make a detailed and critical evaluation of both the experimental informations and the physical model. First some statistical analysis is made of the deviations for each variable z_j: mean value, standard deviation, confidence intervals. If experimental points are very numerous, one can also test the nature of the distribution of deviations. Ideally, the mean should be zero, the σ's equal to assumed value, and the distribution of deviations, gaussian. This test is seldom practical, but it is generally useful to plot the deviations versus x_1. If the points are distributed close to a curve which is different from the Ox_1 axis, it indicates either a lack of flexibility of the model, or systematic error in one or several observed variables, or incorrect data points. If all deviations are scattered around the Ox_1 axis with a normal distribution and if the standard deviations are very different from the assumed σ's, it means that the experimental uncertainties were incorrect. The following examples illustrate the application of such an error analysis to the evaluation of the model and experimental data.

FLEXIBILITY OF THE MODEL

The 15 isothermal vapor-liquid equilibrium data points of Brown and Smith (1954) for the system acetonitrile (1)—tetrachloromethane (2) at 45°C, including the vapor pressure for each component, were used in the reduction of data. The following experimental errors were assumed for x_1, y_1, P, T:

$\sigma(x_1) = 3(10^{-4})$ $\sigma(y_1) = 4(10^{-4})$ $\sigma(T) = 0.10°\text{C}$
$\sigma(P) = 0.20$ mm Hg $(0.05\% < \sigma(P)/P < 0.10\%)$

A first reduction was made by maintaining the NRTL parameter α_{12} at the constant value 0.20. The two adjusted energy parameters and their standard deviations are

$$C_{21} = 910 \qquad \sigma(C_{21}) = 4$$
$$C_{12} = 367 \qquad \sigma(C_{12}) = 3$$

The correlation coefficient between these parameters defined as the ratio of cov. (C_{21}, C_{12}) over the product $\sigma(C_{21}) \cdot \sigma(C_{12})$ is

$$\text{corr.}\ (C_{21}, C_{12}) = -0.94$$

Figure 1A shows the deviations calculated for each experimental variable: the dashed lines indicate the limits corresponding to the assumed uncertainties. The $(\Delta z_j, x_1)$ plots are well out of the range of the assumed experimental errors.

In a second reduction three NRTL parameters were adjusted. The results obtained are listed (parameters, their standard deviation calculated on the basis of the assumed experimental errors, and their correlation coefficients):

$$C_{21} = 1040 \qquad \sigma(C_{21}) = 6$$
$$C_{12} = 675 \qquad \sigma(C_{12}) = 4$$
$$\alpha_{12} = 0.5047 \qquad \sigma(\alpha_{12}) = 0.0024$$

corr. $(C_{21}, C_{12}) = 0.46$; corr. $(C_{21}, \alpha_{12}) = 0.67$; corr. $(C_{12}, \alpha_{12}) = 0.92$

Figure 1B shows the corresponding deviations. The reduction in dispersion is such for all deviations that most of the points are distributed within the limits of the experimental errors. Nevertheless the points still seem to gather along a regular curve slightly different from the Ox_1 axis; therefore, the model could still be refined. Figures 2 and 3, respectively, show the activity coefficients with these three adjusted parameters and the (P, x_1) and (P, y_1) equilibrium diagrams.

CORRELATED PARAMETERS

It was previously shown how the variance-covariance matrix of the parameters $\mathcal{VAR}(\mathbf{C})$ could be obtained from the experimental uncertainties in the measured variables. A correlation coefficient very close to unity between two parameters indicates redundancy. It is interesting to reduce the number of parameters in this case by using the most significant linear combinations of C_j's as parameters. If ω_k $(k = 1, \ldots, m)$ are the eigenvalues of matrix $\mathcal{VAR}(\mathbf{C})$ associated with the eigenvectors $\mathbf{V}_k$, it can be shown (Appendix B) that the m linear combinations χ_k of the optimal parameters defined by

$$\chi_k = \sum_{j=1}^{m} V_{kj}\, C_j \tag{11}$$

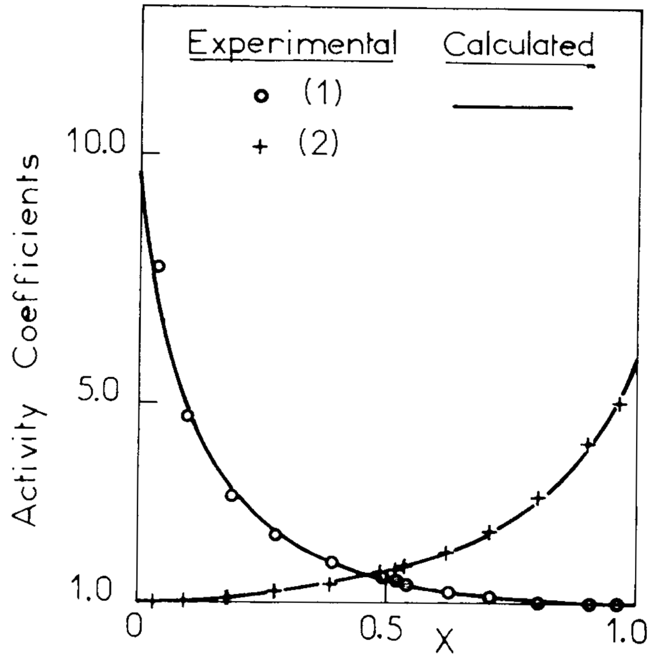

Fig. 2. System acetonitrile (1)—tetrachloromethane (data from Brown and Smith, 1954). Experimental and calculated values of the activity coefficients of each component in the liquid phase. NRTL parameters: $C_{21} = 1039.89$, $C = 675.08$, $\alpha_{12} = .5047$.

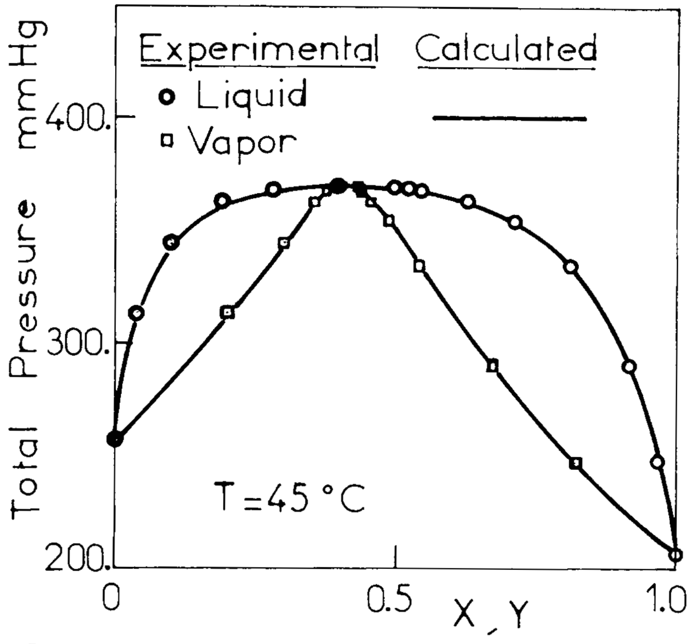

Fig. 3. System acetonitrile (1) tetrachloromethane (2). Total pressure versus composition at equilibrium (data from Brown and Smith, 1954).

are statistically independent, with variances ω_k. The smallest value ω_k is related to the combination of parameters which is known with most accuracy. The confidence region of the calculated parameters is the hyperellipsoid:

$$\mathbf{C}^t \cdot \mathcal{VAR}^{-1}(\mathbf{C}) \cdot \mathbf{C} = \beta^2 \qquad (12)$$

where the number β is related to a probability level.

To illustrate this discussion, the 32 isobaric data points of Ridgway and Butler (1967) for the system benzene (1)—cyclohexane (2) were analyzed using the vapor pressures from the API tables (1971). Two parameters only were adjusted, α_{12} being kept at the value 0.30. The following errors were assumed in a first reduction.

$$\sigma(x_1) = 0.001 \quad \sigma(y_1) = 0.001$$
$$\sigma(T) = 0.10°\text{C} \quad \sigma(P)\ [0.50 \text{ mm Hg}]$$

The resulting parameters are

$$C_{21} = -14 \qquad \sigma(C_{21}) = 19$$
$$C_{12} = -257 \qquad \sigma(C_{12}) = 21$$

The correlation coefficient is −0.99. The observed deviations between calculated and measured properties are given in Figure 7A. They have random distributions with zero means and standard deviations approximately equal to experimental uncertainty. Table 1 gives S, mean values, and standard deviations for two other couples of parameters indicated by Figure 8. In the first reduction, the calculated eigenvalues and eigenvectors are given below:

$$\omega_1 = 795 \qquad \mathbf{V}_1 = \begin{bmatrix} -0.6578 \\ 0.7531 \end{bmatrix}$$
$$\omega_2 = 2.46 \qquad \mathbf{V}_2 = \begin{bmatrix} 0.7531 \\ +0.6578 \end{bmatrix}$$

It can be seen in this example that the most important adjusting parameter is the combination ($0.7531\ C_{21} + 0.6578\ C_{12}$); it is not necessary to introduce two energy parameters in this case. It was observed that strong correlations between NRTL energy parameters were generally associated with weakly nonideal systems. This weakness is common in models incorporating two energy parameters $\epsilon_{12} - \epsilon_{11}$ and $\epsilon_{21} - \epsilon_{22}$ and not the exchange energy $2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$ only, when they are applied to not too strongly nonideal systems.

Models having only one adjustable energy parameter, like those proposed by Bruin and Prausnitz (1971), Tassios (1971), Renon (1974) are better in this case. In these models ϵ_{ii} and ϵ_{jj} are derived from pure substance properties.

INDIVIDUAL INCORRECT POINTS

Sixteen isothermal points were measured by Schäfer and Rall (1958) for the system acetone (1)—*n*-hexane (2). Vapor pressures are also given by the authors. The assumed experimental errors are

$$\sigma(x_1) = 5(10^{-4}) \quad \sigma(y_1) = 5(10^{-4}) \quad \sigma(T) = 0.10°\text{C}$$
$$\sigma(P) = 1.0 \text{ mm Hg} \quad (0.15\% < \sigma(P)/P < 0.30\%)$$

The three NRTL parameters obtained are

$$C_{21} = 623 \qquad \sigma(C_{21}) = 9$$
$$C_{12} = 743 \qquad \sigma(C_{12}) = 6$$
$$\alpha_{12} = 0.5272 \qquad \sigma(\alpha_{12}) = 0.0079$$

TABLE 1. DATA REPRESENTATION FOR SEVERAL PAIRS OF CORRELATED PARAMETERS

				Mean values				Standard deviations			
Set	C_{21}	C_{12}	S	Δx_1 %	Δy_1 %	$\Delta P/P$ %	ΔT°C	Δx_1 %	Δy_1 %	$\Delta P/P$ %	ΔT°C
1	−13.54	256.62	85.1	0.047	−0.046	0.007	−0.026	0.075	0.075	0.019	0.059
2	5	235	86.6	0.042	−0.039	0.008	−0.032	0.079	0.079	0.019	0.058
3	−32	274	90.6	0.052	−0.054	0.011	−0.055	0.071	0.073	0.019	0.064

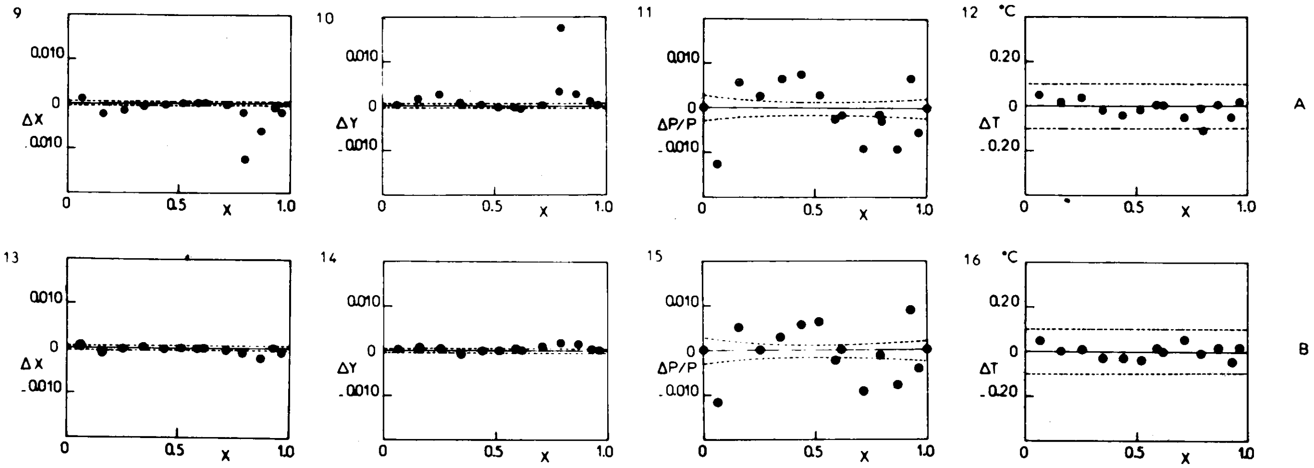

Fig. 4. Acetone (1)—*n*-hexane (2). A—effect of an individual erroneous point on the calculated deviations; B—reduction without this point.

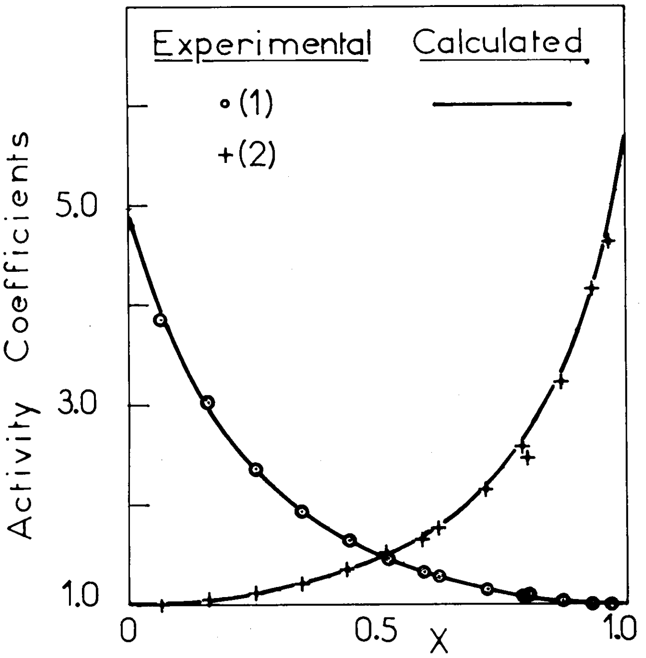

Fig. 5. System acetone (1) *n*-hexane (2). Activity coefficients versus mole fractions in the liquid phase (data from Schäfer and Rall, 1958). NRTL parameters: $C_{21} = 599.68$; $C_{12} = 715.44$; $\alpha_{12} = 0.4849$.

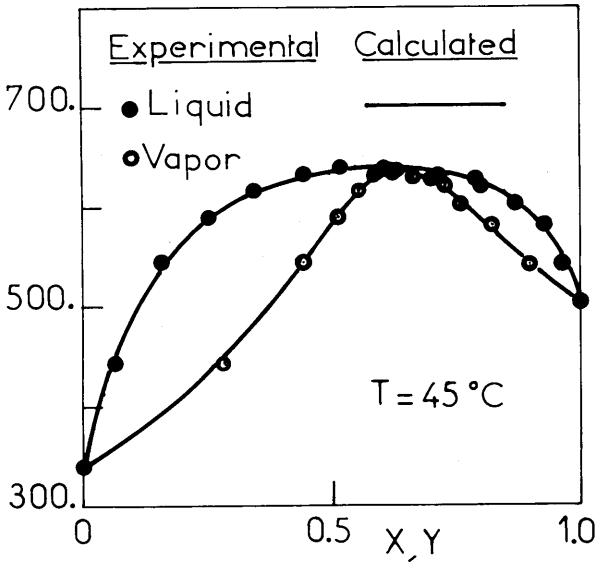

Fig. 6. System acetone (1) *n*-hexane. Total pressure versus composition in both phases (data from Schäfer and Rall, 1958).

The correlation of Tsonopoulos (1974) was used for the fugacity coefficients. Figure 4A shows the calculated deviations. It appears that the experiment corresponding to $x_1 = 0.8022$ gives much more significant deviations on x_1 and y_1 than the other points. The experimental activity coefficients also exhibit deviation for this composition as shown in Figure 5. Because the experimental value of y_1 is so much above the calculated value that it is closer to the composition of liquid, one hypothesize a back-mixing of liquid during sampling in the dynamic still or a sampling error. A reduction omitting this point gives the following parameters:

$$
\begin{aligned}
C_{21} &= 600 & \sigma(C_{21}) &= 11\\
C_{12} &= 715 & \sigma(C_{12}) &= 9\\
\alpha_{12} &= 0.4849 & \sigma(\alpha_{12}) &= 0.0126
\end{aligned}
$$

Figure 4B shows the corresponding deviations. All deviations except on variable P lie approximately within the limits corresponding to the assumed experimental errors. Figure 5 is a plot of γ_1 and γ_2 vs. x_1 and Figure 6, P vs. x_1 and y_1.

INFLUENCE OF EXPERIMENTAL ERRORS ON THE DISTRIBUTION OF THE CALCULATED DEVIATIONS

Three reductions of experimental data for the system benzene (1)—cyclohexane (2) were carried out. The first was presented in the previous section correlated parameters; the errors in x_1 and y_1 were overestimated ($\sigma(x_1) = \sigma(y_1) = 0.001$) and Figure 7A shows that the calculated deviations in P and T are close to zero compared with those in x_1 and y_1. In a second reduction the errors in x_1 and y_1 were decreased assuming reasonable values according to analytic method ($\sigma(x_1) = \sigma(y_1) = 0.0005$). The deviations obtained are practically unchanged. In a third reduction the errors in x_1 and y_1 were maintained at the value 0.001, but the assumed error in pressure was multiplied by a factor 4. The deviations obtained (Figure 7B) agree better with given errors. The corresponding parameters obtained in each reduction are listed in Table 4. This example illustrates the importance of the correct estimation of experimental errors; such estimation should be included in papers presenting vapor-liquid equilibrium results as it is in tables of the *International Data Series* (1973).

EFFECT OF AN ERRONEOUS VAPOR PRESSURE ON THE DEVIATION ON EACH MEASURED QUANTITY

The calculated deviations may be drastically changed if erroneous vapor pressures are used in the reduction, and unfortunately data are often given without measured vapor

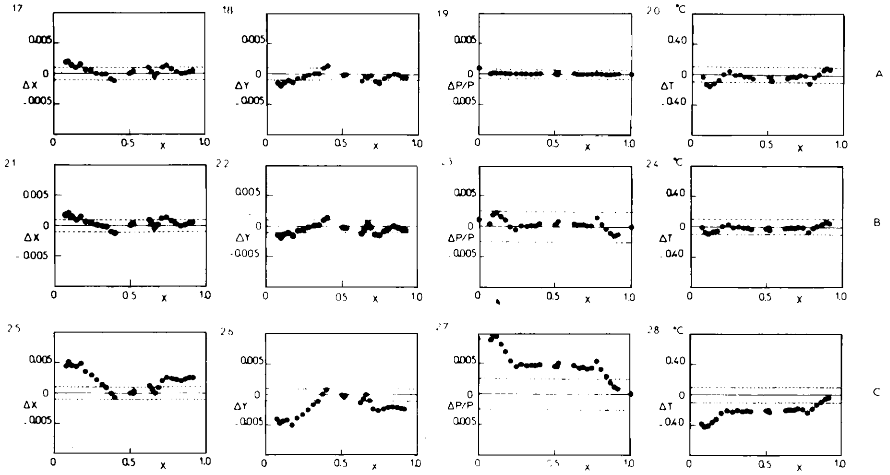

Fig. 7. System benzene (1)—cyclohexane (2) Data from Ridgeway and Butler (1967). A—deviations obtained with two parameters adjusted; B—better distribution by increasing the error in P; C—results in the case of a bad vapor pressure for cyclohexane.

pressures. This omission may be an important reason for data inconsistency, and this problem has already been pointed out by Van Ness et al. (1973). This type of inconsistency can be easily detected by this new method; it influences all deviations and the values of the calculated parameters.

The sample example benzene (1)—cyclohexane (2) was used and the vapor pressure of cyclohexane was arbitrarily decreased by 2.5% in the reduction. The parameters are considerably changed:

$$C_{21} = 348. \text{ instead of } -14$$
$$C_{12} = -84. \text{ instead of } 257$$

Deviations are indicated by Figure 7C and exhibit a characteristic inconsistency for P and T values, which become important when x_1 approaches the zero value (pure cyclohexane). This inconsistency could not be reduced by a more flexible model. When no vapor pressure is given or when the values appear to be in error, the authors would recommend to include the unknown vapor pressure in the adjustable parameters.

Table 2. Values of x_1 for the Experimental Points Used in the Fittings Where the Number of Points is Reduced

Data from Kraus and Linek (1971)

System Acetone (1)—Benzene (2).

x_1 Number of points	12	8	6	4	2
0.0610	+	+	+		
0.1035	+				
0.1608	+	+	+	+	+
0.2607	+				
0.3233	+	+	+	+	
0.3734	+	+			
0.4629	+	+	+	+	+
0.5334	+				
0.5885	+	+	+		
0.7661	+	+			
0.8795	+	+	+	+	
0.9474	+				

INFLUENCE OF THE NUMBER OF EXPERIMENTAL POINTS

Data from Kraus and Linek (1971) on the system acetone (1)—benzene (2) at 30°C (12 binary points) were used to show the influence of the number of experimental points on the reduction. The authors give their own vapor pressure equation for acetone, while the equation given by the API tables was used for benzene.

Experimental errors in x_1 and y_1 were taken as 0.001 according to Kraus and Linek claim of reading the refractive index to ± 0.0001, this quantity varying by 0.14 over the composition range. Some points were taken away so that the remaining data were evenly distributed according to concentration. Values of x_1 used are given in Table 2. Values of the parameters which were obtained and their standard deviations are given in Table 3, along with the corresponding individual deviations for each experimental variable on the basis of 12 experiments. The results of Table 3 show that the mean and standard deviations in each measured variable do not change much when the number of experimental points taken into account in the reduction is decreased from 12 to 4. The errors in the

Table 3. Influence of the Number of Experimental Points Used on the Reduction with the Following Experimental Errors (NRTL Parameter $\alpha_{12} = 0.40$)

$\sigma(x_1) = \sigma(y_1) = 0.001$ $\sigma(P) = 0.15$ mm Hg $\sigma(T) = 0.03°C$

System Acetone (1) Benzene (2) Data from Kraus and Linek (1971) 2 parameters adjusted

No. of points	S cal^{td} for 12 points	NRTL parameters obtained with N points C_{21}	$\sigma(C_{21})$	C_{12}	$\sigma(C_{12})$	Mean values of the deviations on each variable Δx_1 %	Δy_1 %	$\Delta P/P$ %	ΔT°C	Standard deviations Δx_1 %	Δy_1 %	$\Delta P/P°$	ΔT°C
12	553	356	34	−58	25	0.00	−0.29	0.23	−0.14	0.17	0.20	0.18	0.06
8	559	331	32	−37	25	0.03	−0.30	0.23	−0.13	0.16	0.21	0.19	0.06
6	569	301	53	−18	45	0.00	−0.33	0.25	−0.15	0.14	0.21	0.20	0.07
4	560	392	98	−82	69	0.01	−0.25	0.22	−0.13	0.20	0.21	0.17	0.06
2	563	390	9800	−85	6500	−0.03	−0.27	0.25	−0.16	0.19	0.20	0.17	0.06

Table 4. System Benzene (1)—Cyclohexane (2). Influence of the Experimental Errors on the Parameters Obtained
Data from Ridgway and Butler (1967)

Reduction	$\sigma(x_1)$	$\sigma(y_1)$	$\sigma(P)$ mm Hg	$\sigma(T)$ °C	C_{21}	C_{12}	α_{12}
1	0.001	0.001	0.50	0.10	−14	257	0.30
2	0.0005	0.0005	0.50	0.10	−17	260	0.30
3	0.001	0.001	2.00	0.10	−14	257	0.30

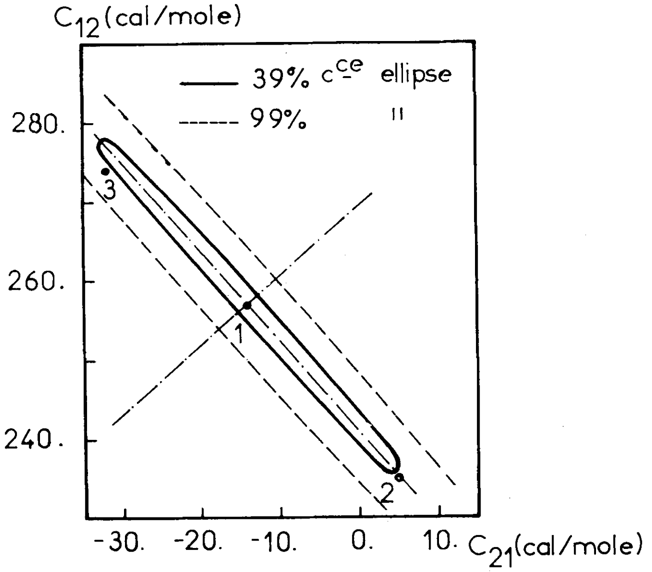

Fig. 8. System benzene (1) cyclohexane (2). Confidence ellipses of the two adjusted NRTL parameters for $\beta = 1$ and $\beta = 3$, the points represent the three sets of parameters in Table 1.

value of the parameters increase steadily. These errors are not very significant for two data points only; the parameter values obtained are not fundamentally different from those calculated with more points because the data are good, but the confidence region predicted on the basis of two points is very large as indicated by the σ's.

This example shows very simply that one does not need many points to obtain a fair representation for data when the model is suitable for this level of accuracy.

CONCLUSION

The method proposed gives the user two main possibilities:

1. To check the validity of binary vapor-liquid equilibrium data.
2. To check the capability of a thermodynamic model to represent these data.

The calculation of the optimal parameters of the model is associated with the determination of their estimated errors, and the confidence region at a given probability level can be estimated. This can avoid the utilization of models with strongly correlated parameters which are not significant. Use can be made of the confidence limits in the values of parameters to estimate those in the output variables of a process.

Deviations on each measured quantity are calculated. The analysis of these deviations can give information relative to both data and model. It is recommended in all cases to draw diagrams giving a plot of the deviations in each variable versus x_1 and to examine if the points are scattered around the Ox_1 axis or on the contrary seem to gather close to a different curve. If the data are numerous, the nature of the distribution can be checked by use of a χ-square test for instance. When the distribution appears to be gaussian and points to be scattered around the Ox_1 axis, the deviations can be compared with the experimental errors. If the standard deviations are close to the assumed uncertainties (obtained from reproducibility tests by the experimentalist himself) the data are good and the reduction is satisfactory. Otherwise there is either a lack of flexibility of the model, or systematic error in one or several measured variables. If such systematic errors occur, they will have an effect on all deviations. Nevertheless a wrong vapor pressure or one single incorrect point will be easily detected in the diagrams. The check on the validity of experimental vapor-liquid measurements is obtained by using a flexible enough model. The present method is a useful help for the experimentalist designing a new vapor-liquid equilibrium still and testing it by a large number of measurements on a well-known system.

A physical chemist, interested in finding the best possible model of representation partly derived from theory, will use the same set of reliable data with experimental errors to compare deviations obtained when changing or modifying the model of representation.

The present method will help the process engineer who must obtain vapor-liquid data which cannot be found in the literature, in choosing the accuracy of determinations and the number of experimental points needed.

It can be pointed out that the method allows the reduction of isothermal data as well as of isobaric data, and no additional information is necessary to check their validity, contrary to the classical consistency tests previously quoted.

Finally the method can be extended to other types of data, incomplete vapor-liquid data ($P - x_1 - T$, $x_1 - y_1 - T$, $P - y_1 - T$), infinite dilution activity coefficients, heats of mixing.

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NOTATION

$\mathfrak{A}$ = matrix of the linear system (8)
$\mathbf{B}$ = coefficients in Equation (8) (vector)
$\mathbf{C}$ = parameters of the thermodynamic model (vector)
$\text{cov}(e_1, e_2)$ = covariance of the two quantities e_1 and e_2: mean value of the product $e_{1k} \cdot e_{2k}$ for a large number of measurements k
$\text{corr}(e_1, e_2)$ = correlation coefficient defined as the ratio of $\text{cov}(e_1, e_2)$ over the product $\sigma(e_1) \cdot \sigma(e_2)$
C_{21}, C_{12} = NRTL energy parameters (cal/mole)
$\mathfrak{D}$ = matrix defined by Equation A5
d = distance between experimental and calculated points defined by Equation (10)
f_l^{0L*} = fugacity of pure component l, in liquid state and zero pressure

$\mathbf{F}$ = coefficients defined by Equation A7 (vector)
g^E = excess Gibbs free energy, cal/mole
m = number of parameters of the thermodynamic model
N_l = Poynting's correction: $\exp(v_l^{0L} \cdot P/RT)$
P = pressure
R = gas constant
r_{li} = residual defined by Equation (4)
S = function of residuals defined by Equation (5)
T = temperature, °K
t_i = deviation term defined by Equation (A2)
$\mathbf{V}_k$ = eigenvector associated with eigenvalue ω_k of matrix $\mathcal{VAR}(\mathbf{C})$
v_l = molar volume of component l
$\mathcal{VAR}(\mathbf{E})$ = variance covariance matrix related to vector $\mathbf{E}$
x_l = liquid phase mole fraction of component l
y_l = vapor phase mole fraction of component l
$\mathbf{z}_i$ = measured variable vector

Greek Letters

α_{12} = NRTL parameter (dimensionless)
β = scalar number
γ_l = activity coefficient
δr_{li} = error in residual r_{li}
$\boldsymbol{\Delta}\mathbf{C}$ = parameter increments (vector)
Δx = deviation on x: difference between the experimental and the calculated value of x
ϵ = energy interaction parameter (cal/mole)
θx = indicates a small variation in x
$\nu(z_j)$ = norm related to variable z_j
$\sigma(x)$ = standard deviation related to x
$\sigma^2(x)$ = variance
τ_{jk} = NRTL parameter (C_{jk}/RT)
ϕ_l = vapor phase fugacity coefficient
χ_k = linear combination of parameters
ω_k = eigenvalue of matrix

Superscripts

E = excess property
L = liquid
0 = pure component
$*$ = reference zero pressure
t = matrix transposition
-1 = matrix inversion

Subscript

1, 2 = relative to one component in the mixture
i indicates an experiment
μ indicates a measurement in experiment
0 refers to the last step of an iterative process

LITERATURE CITED

Abrams, D. S., Ph.D. thesis, Univ. of California, Berkeley (1974).

Bard, Y., and L. Lapidus, "Kinetics analysis by digital parameter estimations," *Catalysis Rev.*, **2**(1), 67 (1968).

Bruin, S., and J. M. Prausnitz, "A one-parameter Equation for the Excess Gibbs Energy of Strongly Non-ideal Liquid Mixtures," *Ind. Eng. Chem. Process Design Develop.*, **10**, 562 (1971).

Brown, I., and F. Smith, "Liquid-Vapour Equilibria. Part V: the System carbon tetrachloride + acetonitrile at 45°C," *Austral. J. Chem.*, **7**, 269 (1954).

Kehiaian, H. V., "International Data Series—Selected Data on Mixtures," Publ. by Thermodynamics Research Center, College Station, Texas (1973).

Kraus, J., and J. Linek, "Liquid-Vapour Equilibrium XLVIII. The systems acetone-benzene, acetone-toluene, benzene-methyl ethyl ketone, methylethyl ketone-toluene and methyl ethyl ketone-ethyl benzene," *Collection Czechoslov, Chem. Commun.*, **36**, 2547 (1971).

Nothnagel, K. H., D. S. Abrams, and J. M. Prausnitz, "Generalized Correlation for Fugacity Coefficients in Mixtures at Moderate Pressures—Application of Chemical Theory of Vapor Imperfections," *Ind. Eng. Chem. Process Design Develop.*, **12**, 25 (1973).

O'Connel, J. P., and J. M. Prausnitz, "Empirical Correlation of Second Coefficients for Vapor-Liquid Equilibrium Calculations," *Ind. Eng. Chem. Process Design Develop.*, **6**, 245 (1967).

Péneloux, A., and R. Deyrieux, personal communication (1973).

Prausnitz, J. M., C. A. Eckert, R. V. Orye, and J. P., O'Connel, *Computer Calculation for Multicomponent Vapor-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, N. J. (1967).

———., *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, Englewood Cliffs, N. J. (1969).

Renon, H., "Extension de la théorie quasi-chimique à des mélanges de molécules de tailles et de formes différentes" C. R. Acad, S.c. Paris, t 278 n° 5 Série B—147 (1974).

Renon, H., and J. M. Prausnitz, "Local compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).

Renon, H., L. Asselineau, G. Cohen, C. Raimbault, *Calcul sur ordinateur des equilibres liquide vapeur et liquide-liquide, Technip.*, Paris (1972).

Ridgway, K., and P. A. Butler, "Some Physical Properties of the Ternary System Benzene-Cyclohexane-n Hexane," *J. Chem. Eng. Data*, **12**, 509 (1967).

Samuels, M. R., D. L. Ulrichson, and F. D. Stevenson, "Interpretation of Overall Area Tests for Thermodynamic Consistency: The Effect of Random Error," *AIChE J.*, **18**, 1004 (1972).

Schäfer, Kl., and W. Rall, "Dampfdruckuntersuchungen und Aktivitätskoeffizienten des Systems Aceton-n Hexan," *Z. Elektrochem.*, **62**, 1090 (1958).

Tassios, D., "A Single Parameter Equation for Isothermal Vapour-liquid Equilibrium Correlations," *AIChE J.*, **17**, 1367 (1971).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *ibid.*, **20**, 263 (1974).

Ulrichson, D. L., and E. D. Stevenson, "Effects of Experimental Errors on Thermodynamic Consistency and on Representation of Vapor-Liquid Equilibrium Data," *Ind. Eng. Chem. Fundamentals*, **11**, 287 (1972).

Van Ness, H. C., *Classical Thermodynamics of Non Electrolyte Solutions*, Pergamon Press, London (1964).

Van Ness, H. C., S. M. Byer, and R. E. Gibbs, "Vapor-Liquid Equilibrium. Part I: An Appraisal of Data Reduction Methods. Part II: Correlations for T-x Data for 15 systems," *AIChE J.*, **19**, 238 (1973).

Wichterle, I., J. Linek, and E. Hála, *Vapor Liquid Equilibrium Data Bibliography*, Elsevier, New York (1973).

Zwolinski, B. J., and R. C. Wilhoit, "Handbook of vapor pressures and heats of vaporization of hydrocarbons and related Compounds," Publ. 101, API Project 44 (1971).

APPENDIX A

The parameters $\mathbf{C}$ of the models are found by minimizing the sum S

$$S = \sum_{i=1}^{n} t_i^2 \tag{A1}$$

$$t_i = [\mathbf{r}_i^t \cdot \mathcal{VAR}(\mathbf{r}_i) \cdot \mathbf{r}_i]^{1/2} \tag{A2}$$

The quantity between brackets is a definite positive quadratic form with respect to residuals. Linearization applied before writing all $\partial S/\partial C_k$ are zero leads to a linear system.

$$\mathcal{A} \cdot \boldsymbol{\Delta}\mathbf{C} = \mathbf{B} \tag{A3}$$

The terms A_{kj} and B_k of matrix $\mathbf{A}$ and vector $\mathbf{B}$ are

$$A_{kj} = A_{jk} = \sum_{i=1}^{n} D_{ij} \cdot D_{ik} \tag{A4}$$

with

$$D_{ij} = (\partial t_i/\partial C_j)_0 \tag{A5}$$

$$B_k = \sum_{i=1}^{n} F_i \cdot D_{ik} \tag{A6}$$

with

$$F_i = -t_{i0} \qquad \text{(A7)}$$

Subscript 0 indicates that the value of this partial derivative is taken with either the values of parameters obtained at the end of the previous iteration or the initial values. In the calculation of each D_{ij}, it is assumed that the terms of matrix $\mathcal{VAR}(\mathbf{r}_i)$ do not vary. In fact, they are parameter dependent and they are recalculated at each step; however, this dependence is small near the optimum and the procedure was found always convergent for all the examples studied.

The F_i's (Equations A6 and A7) are deviation terms which can be considered as random variables generated from a set of measured variables. If one assumes a normal distribution for t_{i0}, it can be shown that $\sigma^2(F_i)$ is unity and $\text{cov}(F_i, F_j)$ is zero because the errors are independent in different experiments. Therefore, the variance-covariance matrix $\mathcal{VAR}(\mathbf{F}_i)$ is the unit matrix when all parameter increments ΔC_k are close to zero. The small variations of parameters θC_k produced by small variations in vector **F** are related by the following equation deduced from (A4) and (A6)

$$\mathcal{D}^t \cdot \mathcal{D} \cdot \boldsymbol{\theta}\mathbf{C} = \mathcal{D}^t \cdot \boldsymbol{\theta}\mathbf{F} \qquad \text{(A8)}$$

where $\mathcal{D}$ is the matrix of which the elements are the D_{ij}'s

$$\mathcal{A} = \mathcal{D}^t \cdot \mathcal{D} \qquad \text{(A9)}$$

It results from (A8) and (A9)

$$\mathcal{A} \cdot \boldsymbol{\theta}\mathbf{C} \cdot \boldsymbol{\theta}\mathbf{C}^t \cdot \mathcal{A} = \mathcal{D}^t \cdot \boldsymbol{\theta}\mathbf{F} \cdot \boldsymbol{\theta}\mathbf{F}^t \cdot \mathcal{D} \qquad \text{(A10)}$$

$$\mathcal{A} \cdot \mathcal{VAR}(\mathbf{C}) \cdot \mathcal{A} = \mathcal{D}^t \cdot \mathcal{VAR}(\mathbf{F}) \cdot \mathcal{D} = \mathcal{A} \qquad \text{(A11)}$$

and finally

$$\mathcal{VAR}(\mathbf{C}) = \mathcal{A}^{-1} \qquad \text{(A12)}$$

APPENDIX B

The variance covariance matrix of parameters $\mathcal{VAR}(\mathbf{C})$ is a symmetrical $m.\ m$ matrix, and, therefore, it has m real eigenvalues ω_k $(k = 1, \ldots, m)$ associated with m eigenvectors $\mathbf{V}_k$ (of elements $V_{k1}, V_{k2}, \ldots, V_{km}$).

Let

$$\chi_k = \sum_{j=1}^{m} V_{kj} \cdot C_j \qquad \text{(B1)}$$

the following equations are deduced

$$\sigma^2(\chi_k) = \mathbf{V}_k^t \cdot \mathcal{VAR}(\mathbf{C}) \cdot \mathbf{V}_k \qquad \text{(B2)}$$

$$\text{cov}(\chi_k, \chi_j) = \mathbf{V}_k^t \cdot \mathcal{VAR}(\mathbf{C}) \cdot \mathbf{V}_j \qquad \text{(B3)}$$

$\mathbf{V}_k$ and $\mathbf{V}_j$ being eigenvectors, it gives

$$\mathcal{VAR}(\mathbf{C}) \cdot \mathbf{V}_k = \omega_k \cdot \mathbf{V}_k \qquad \text{(B4)}$$

$$\mathcal{VAR}(\mathbf{C}) \cdot \mathbf{V}_j = \omega_j \cdot \mathbf{V}_j \qquad \text{(B5)}$$

from (B2), (B3), (B4), and (B5), it is deduced

$$\sigma^2(\chi_k) = \omega_k \mathbf{V}_k^t \cdot \mathbf{V}_k \qquad \text{(B6)}$$

$$\text{cov}(\chi_k, \chi_j) = \omega_j \cdot \mathbf{V}_k^t \cdot \mathbf{V}_j \qquad \text{(B7)}$$

As the vectors $\mathbf{V}_k$ and $\mathbf{V}_j$ (with $k \neq j$) are orthogonal and if it is assumed that they are normalized, the following equations are verified:

$$\sigma^2(\chi_k) = \omega_k \qquad \text{(B8)}$$

$$\text{cov}(\chi_k, \chi_j) = 0 \qquad \text{(B9)}$$

These last equations indicate that it is possible to find some combinations of parameters the errors of which are independent. The eigenvectors $\mathbf{V}_k$ give the eigendirections of the confidence hyperellipsoid (Ω):

$$\mathbf{C} \cdot \mathcal{VAR}^{-1}(\mathbf{C}) \cdot \mathbf{C} = \beta^2$$

the center of (Ω) being the optimal point $\mathbf{C}^{\text{opt.}}$ previously calculated.

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Interphase Mass and Heat Transfer in Pulsatile Flow

A study on the effects of flow pulsations on interphase mass or heat transfer has been made. The situation corresponds to fully developed flow in a long conduit with a periodic pressure gradient at amplitudes which cause flow pulsations without flow reversal. It is shown that the basic three-parameter formulation can be reduced to a one-parameter problem in the boundary layer formulation. Solutions are developed over wide ranges of the parameters in both the basic and the boundary layer formulations.

The boundary approach gives accurate results over wide ranges of the parameters. Pulsations cause increases in the time-averaged interphase flux at intermediate values of a composite frequency-space variable. However, at small values of this variable the pulsations cause a decrease in the flux such that the overall space-averaged flux is always decreased.

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SCOPE

For the past twenty years a great deal of research has been directed at the question of whether pulsations in the fluid velocity in heat and mass transfer devices can improve the performance of these devices. Investigations of this problem, both theoretical and experimental, have led to numerous contradictions, and there is still confusion over the important basic question as to the circumstances in which pulsations cause an increase or decrease in the average interphase mass or heat transfer.

Interphase mass and heat transfer are of interest in many areas of engineering, and the effect of flow pulsations on the interphase flux clearly is of interest in each

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