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Interpretation of Overall Area Tests for Thermodynamic Consistency: The Effect of Random Error

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Methods are developed and illustrated for determining the amount of nonsatisfaction of the overall area (integrated Gibbs-Duhem equation) test for vapor-liquid equilibrium data that is to be expected on the basis of random experimental uncertainties. Data which satisfy the overall test within these limits, as well as the local area test, are said to be consistent within the bounds established by their experimental uncertainties, while data which do not are said to show significant systematic error and hence are termed inconsistent.

SCOPE

Experimental vapor-liquid data are frequently checked for internal consistency by means of the Gibbs-Duhem equation (either in its differential or integral form). Unfortunately, no set of vapor-liquid data will exactly satisfy the Gibbs-Duhem equation. Such lack of agreement may arise from systematic errors due to failure of the experimental procedure or instrumentation and random experimental uncertainties because of the finite resolution of the experimental measurements. Although random measurement uncertainties may lead in many cases to the same form of incorrect results as do systematic errors, a set of data which are subject to essentially random uncertainties should not be rejected as inconsistent because they do not satisfy the Gibbs-Duhem equation. One may legitimately claim that these random uncertainties make the data of questionable value (particularly if there are insufficient data to allow the experimental uncertainties to be reduced by statistical averaging techniques). But this is a considerably different statement than saying that the data are inconsistent. The inconsistent label should be applied only to those data which exhibit systematic error. These data are of considerably lower value since no averaging techniques are capable of reducing the effects of systematic errors. A previous paper describes the propagation of experimental uncertainties in the application of the differential Gibbs-Duhem equation. In this paper a procedure is developed for determining the nonsatisfaction of the integral Gibbs-Duhem equation that is attributable solely to random experimental uncertainties. Data which show significantly more nonsatisfaction than this are termed inconsistent. The procedure is illustrated by application to ten sets of experimental vapor-liquid equilibrium data selected from the literature.

CONCLUSIONS AND SIGNIFICANCE

In this work it is assumed that all experimentally determined quantities are subject to small, randomly distributed errors. It is also assumed that these errors follow a normal distribution whose statistical behavior is totally defined if the mean and standard deviation of the measured quantity are known.

The integral form of the Gibbs-Duhem equation may be expressed in the form:

$$\int_a^b \left[\sum_{i=1}^{c} (x_i \, d\ln \gamma_i) + \frac{\Delta \underline{H}_m}{RT^2} dT - \frac{\Delta \underline{V}_m}{RT} dP \right] = F(a,b) \quad (1)$$

For data which obey the Gibbs-Duhem equation exactly, $F(a, b)$ will vanish. If the data do not satisfy the Gibbs-Duhem exactly, then the magnitude of $F(a, b)$ is a quantitative measure of this nonsatisfaction. Since only a finite quantity of experimental data will be available for evaluation of the integral in Equation (1) some form of numerical integration will be needed. Rather than use highly complex formulae for integration over a large range of composition which includes many data points, the analysis begins by considering a pair of adjacent data points (a_j, b_j)

$$\int_{a_j}^{b_j} \left[\sum_{i=1}^{c} x_i \, d\ln \gamma_i + \frac{\Delta \underline{H}_m}{RT^2} dT - \frac{\Delta \underline{V}_m}{RT} dP \right] = F(a_j, b_j) = F_j \quad (2)$$

where F_j is termed the local area defect. By summing the local area defects across the entire composition range (a, b) the overall area defect is obtained.

The integrals in the local area defect are evaluated by means of the trapezoid rule. The propagation of error formula is now applied to the numerical integration algorithm to predict the expected standard deviation in the local area defect σ_{F_j} in terms of the standard deviations in the measured quantities x, y, P, and T. Once the local area defects and their predicted standard deviations are known, the total area defect and its predicted standard deviation are obtained from

$$\text{total area defect} = \sum_{j=1}^{N} F_j \quad (3)$$

$$\sigma^2_{\Sigma F_j} = \sum_{j=1}^{N} \sigma^2_{F_j} \quad (4)$$

From the value of the predicted standard deviation in the total area defect it is now possible to determine whether or not the total area defect is significantly greater than zero. It is shown that if the actual area defect is greater than 1.65 times the expected standard deviation in the area defect there is less than a 10% probability that the data under investigation are subject only to the random measurement errors postulated at the beginning of the analysis. Since one would usually not reject an occurrence as statistically unlikely until its probability of occurrence was less than 10%, any data set with a total area defect less than 1.65 times its expected standard deviation would be accepted as being subject only to the postulated random measurement errors. On the other hand, a data set with a total area defect greater than two or three times its standard deviation would surely be rejected as being subject to systematic errors. For values of $\Sigma F_j/\sigma_{\Sigma F_j}$ between 1.65 and ~2.5 the decision to accept or reject the data set is not clearcut and other factors would have to be included in the overall evaluation of the data set. (For example, are there several particular data points which contribute a large fraction of the total area defect, and hence should probably be ignored? In cases of this nature, the running area test also described in the paper may be of some assistance).

Previously suggested criterion for accepting or rejecting experimental vapor-liquid equilibrium data on the basis of the Gibbs-Duhem equation have relied on some vaguely defined maximum error bounds. Although this may not cause serious difficulty when the data are clearly acceptable, or unacceptable, many sets of data fall some place between these limits. In such situations the statistical interpretations presented herein offer valuable guidelines for the evaluation of experimentally determined activity coefficients by means of the Gibbs-Duhem equation.

THEORY

In this discussion methods for determining the amount of nonsatisfaction of the integral Gibbs-Duhem equation that is attributable solely to random experimental error will be developed and examined. It is assumed in the remainder of this discussion that all experimentally determined quantities are subject to small, randomly-distributed errors. It is assumed that these errors follow a normal distribution whose statistical behavior is totally defined if the mean and standard deviation σ of the measured quantity are known.

If the differential and integral forms of the Gibbs-Duhem equation are expressed as

$$\sum_{i=1}^{c} (x_i \, d\ln \gamma_i) + \frac{\Delta \underline{H}_m}{RT^2} dT - \left(\frac{\Delta \underline{V}_m}{RT} \right) dP = F' \quad (1)$$

and

$$\int_a^b \left[\sum_{i=1}^{c} (x_i \, d\ln \gamma_i) + \frac{\Delta \underline{H}_m}{RT^2} dT - \left(\frac{\Delta \underline{V}_m}{RT} \right) dP \right] = F(a,b) \quad (2)$$

then F' and $F(a, b)$ will vanish for data that satisfy the Gibbs-Duhem equation identically. If the data do not satisfy these equations exactly, then the magnitude of F' or $F(a, b)$ is a quantitative measure of the nonsatisfaction of the equations. Once numerical algorithms are chosen for the evaluations of the derivatives and integrals in Equations (1) and (2) it will be possible to apply the theory of propagation of errors to these algorithms and thereby predict the standard deviations in F' and $F(a, b)$ that should be expected solely on the basis of the experimental uncertainties in the quantities (P, T, x, and y) from which the F' and $F(a, b)$ have been determined.

Since numerical algorithms for differentiation are subject to severe truncation errors, while those for integration are not as subject to severe truncation errors, this discussion will be limited to the integral form [Equation (2)] of the Gibbs-Duhem equation. In addition, rather than develop highly complex formulae for integration over a large range of composition which includes many data points, integration between the jth set of adjacent data points (a_j, b_j) will be the starting point:

$$\int_{a_j}^{b_j} \sum_{i=1}^{c} x_i \, d\ln \gamma_i + \int_{a_j}^{b_j} \frac{\Delta \underline{H}_m}{RT^2} \, dT - \int_{a_j}^{b_j} \frac{\Delta \underline{V}_m}{RT} \, dP = F(a_j, b_j) = F_j \quad (3)$$

where F_j is the local area defect.

Equation (3) has been referred to as the local-area test by Ulrichson and Stevenson (1972). By summing over all such local areas between $x_i = a$ and $x_i = b$ the overall area test may be obtained. If the uncertainty associated with the local area can be expressed in terms of the uncertainties in x, y, P, and T, then it will be possible to determine the uncertainty associated with the sum of these local areas by direct application of the propagation of error formulae to the sum.

Although many numerical algorithms are available for evaluation of the local integrals in Equation (3), the simple trapezoid rule will be used herein. Ulrichson and Stevenson (1972) report that this integration procedure is acceptably accurate for reasonably-sized integration intervals. In addition, the uneven increments in the experimental values of $\ln \gamma_i$ make use of multipoint integration formulae rather cumbersome. For the trapezoid rule integration, Equation (3) is expressed as

$$\sum_{i=1}^{c} \left[\left(\frac{x_{ia} + x_{ib}}{2} \right) \left(\ln \frac{\gamma_{ib}}{\gamma_{ia}} \right) \right] + \frac{1}{2} \left[\left(\frac{\Delta \underline{H}_m}{RT^2} \right)_a + \left(\frac{\Delta \underline{H}_m}{RT^2} \right)_b \right] [T_b - T_a] - \frac{1}{2} \left[\left(\frac{\Delta \underline{V}_m}{RT} \right)_a + \left(\frac{\Delta \underline{V}_m}{RT} \right)_b \right] [P_b - P_a] = F_j \quad (4)$$

where the j's have been dropped for convenience.

The propagation of error formulae may now be applied to determine the expected standard deviation in the local area defect σ_{F_j} in terms of the standard deviations in the measured quantities x, y, P, and T. This analysis has been performed by Ulrichson and Stevenson (1972). [If the σ_x, σ_y, σ_P, and σ_T needed for this analysis have not been determined during the experiments under investigation, they may be estimated by means of procedures suggested by Samuels et al. (1972).] With the values of F_j and σ_{F_j} so calculated it is now possible to check whether or not the values of F_j are in fact randomly distributed with standard deviation σ_{F_j}. This is an extremely valuable test on the randomness of the experimental errors which should always be checked before the overall test is attempted. By means of the local test it is frequently possible to pick up local inconsistencies or compensating errors which the overall test may miss.

Once the local area defects and their expected standard deviations have been estimated, the total area defect ΣF_j is calculated from the sum of the individual area defects. The expected standard deviation in the sum is obtained from the propagation of error formula applied to the sum:

$$\sigma^2_{\Sigma F_j} = \sum_{j=1}^{N} \sigma^2_{F_j} \quad (5)$$

From the value of the standard deviation in the total area defect, it is now possible to determine whether or not this quantity is significantly different from zero. If it is, the consistency of the set of data should be questioned. If not, there is no basis for rejection of the data due to nonsatisfaction of the Gibbs-Duhem equation. If as postulated, the experimental data under investigation are subject only to small randomly-distributed measurement errors, then the value of the total area defect should be one member from a randomly distributed set of area defects that would be obtained if the whole set of experimental measurements were repeated many times. The relative distribution of area defects obtained from these duplicate sets of experiments should follow the normal distribution curve with a mean of zero and a standard deviation of $\sigma_{\Sigma F_j}$. The probability of any one measured value of the area defect falling within the range $\pm \alpha \sigma_{\Sigma F_j}$ is simply the fraction of the total area under the normal distribution function that occurs within the bounds of $\pm \alpha \sigma_{\Sigma F_j}$. Thus, for example, the likelihood of any given total area defect falling within $\pm \sigma_{\Sigma F_j}$ is 68.3%, while the likelihood of its falling outside this range and still being from the postulated normal distribution of area defects is 31.7%. Usually one would not reject an occurrence as being statistically unlikely unless its probability of occurrence was less than about 10%. That is, for the problem at hand one would not reject a ΣF_j as being significantly different from zero unless ΣF_j was greater in magnitude than about 1.65 $\sigma_{\Sigma F_j}$.

The overall area test of Equation (2) can be converted to a somewhat more familiar form if the first term in the left-hand side is integrated by parts. For binary mixtures this partially integrated equation may be written in a particularly convenient form:

$$\int_a^b \left[\ln \frac{\gamma_1}{\gamma_2} - \frac{\Delta \underline{H}_m}{RT^2} \frac{dT}{dx_1} + \frac{\Delta \underline{V}_m}{RT} \frac{dP}{dx_1} \right] dx_1 = - \sum_{j=1}^{N} F_j + Q_a - Q_b \quad (6)$$

where

$$Q = \sum_{i=1}^{2} x_i \ln \gamma_i \, .$$

If a and b correspond to pure components, and the normal choice of activity coefficients ($\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$) are used, then $Q_a = Q_b = 0$ and Equation (6) reduces to the nonisobaric, nonisothermal version of the familiar total area test. The predicted standard deviation σ_A in the area calculated from Equation (6) is obtained from the propagation of error formula

$$\sigma^2_A = \sigma^2_{\Sigma F_j} + \sigma^2_{Q_b} + \sigma^2_{Q_a} \quad (7)$$

where

$$\sigma_Q^2 = \left[\left(\ln \frac{\gamma_1}{\gamma_2} \right)^2 \sigma_x^2 + \left(\frac{x_1}{y_1} - \frac{x_2}{y_2} \right)^2 \sigma_y^2 + \frac{1}{P^2} \sigma_P^2 + \left(- \frac{x_1}{\gamma_1} \frac{d\ln P_1'}{dT} - \frac{x_2}{\gamma_2} \frac{d\ln P_2'}{dT} \right)^2 \sigma_T^2 \right] \quad (8)$$

Thus the standard deviation in the integral of Equation

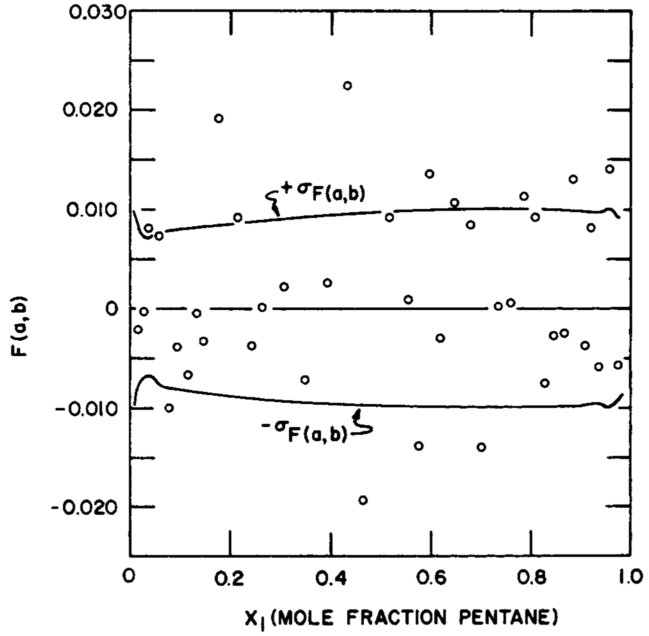

Fig. 1. Local area test for data of Meyers.

(6) may be estimated from Equations (7) and (8). This estimation will not be exact, however, unless the integral has actually been calculated from ΣF_j, Q_a, and Q_b as suggested in Equation (6). Thus, for example, the standard deviation associated with a graphical integration of

$$\int_a^b \left[\ln\frac{\gamma_1}{\gamma_2} - \frac{\Delta \underline{H}_m}{RT^2}\frac{dT}{dx_1} + \frac{\Delta \underline{V}_m}{RT}\frac{dP}{dx_1} \right] dx_1$$

would not be identical to that indicated by Equations (7) and (8), but should not be far from this value. The exact value of the standard deviation in this integral could be evaluated, once a specific algorithm for numerical integration were chosen, by means of the propagation of error formula. However, the amount of calculations involved in this operation is essentially the same as that for the suggested direct integration of Equation (3). (Either calculation can be performed in a matter of seconds or less on a digital computer). In addition the value of the intermediate calculations in checking the random nature of the function F_j would be lost. Thus the direct integration of

$$\left[\ln\frac{\gamma_1}{\gamma_2} - \frac{\Delta \underline{H}_m}{RT^2}\frac{dT}{dx_1} + \frac{\Delta \underline{V}_m}{RT}\frac{dP}{dx_1} \right],$$

although long practiced, has no particular advantage over the integration in Equation (3), and in fact is significantly less useful.

DISCUSSION

The activity coefficient composition data of Meyers (1955) for the binary system Pentane (1)—Benzene (2) at 760 mm Hg will be used for illustrative purposes. These data have been examined by means of other consistency tests in the past and serve as a useful illustration of the dangers inherent in the improper use of statistics. The local areas F_j and their expected standard deviations for this data are presented in Figure 1. The expected standard deviations in F_j, σ_{F_j}, have been evaluated on the basis of $\sigma_x = \sigma_y = 0.002$, $\sigma_T = 0.16$°C, and $\sigma_P = 0.2$ mm Hg, as suggested by the procedure of Samuels et al. (1972). Heats of mixing for the system pentane-benzene have been estimated from the heats of mixing for the systems hexane-benzene and heptane-benzene. Although these values are at best an estimate, the heat of mixing term in Equation (3) is quite small, and hence even a relatively large error in $\Delta \underline{H}_m$ will not change the values of F_j to any significant degree. The total area defect was found to be

$$\sum_{i=1}^{N} F_j = 0.069$$

for the 39 data points involved. The expected standard deviation in this quantity predicted by Equation (5) is

$$\sigma_{\Sigma F_j} = 0.057$$

The ratio $\alpha = \sum_{i=1}^{N} F_i/\sigma_{\Sigma F_j}$ calculated for this data is then $\alpha = 1.21$. Since this value is below 1.65 there is greater than a 10% likelihood that this value would be obtained from the postulated random distribution. Thus, by the criterion discussed earlier there is no basis for rejecting these data as inconsistent.

Table 1 summarizes the results of the overall area test as applied to 10 sets of data selected at random from the literature. Figures 2 and 3 summarize the local area test applied to the same data. The only major criterion used in choosing these data sets was that they contain enough data points to allow the statistical analyses developed herein to apply. Examination of the table shows that the ratio $\Sigma_{F_j}/\sigma_{\Sigma F_j}$ does appear (as assumed) to be reasonably randomly distributed. Of the ten sets of data tested, only those of Ho and Lu (1963) show an area defect which has less than a 10% chance of being part of the proposed random distribution and hence might be considered significantly different from zero. Thus, although the data of Ho and Lu appear to satisfy the local area test as shown in Figure 2, there is enough error in the overall area to suggest a small systematic error. However, even here, the decision is borderline, and the data might still be used in applications where its questionable accuracy is acceptable. A further check on the data of Ho and Lu could be obtained by considering the area defect for the composition range $0 < x_1 < x$, as a function of x, and the expected standard deviation in this area defect, as shown in Figure 3. The area defect does not fluctuate about zero as it should, but has a definite positive trend which is somewhat greater than $\sigma_{\Sigma F_j}$. Thus we are again lead to the conclusion that this data appears to be subject

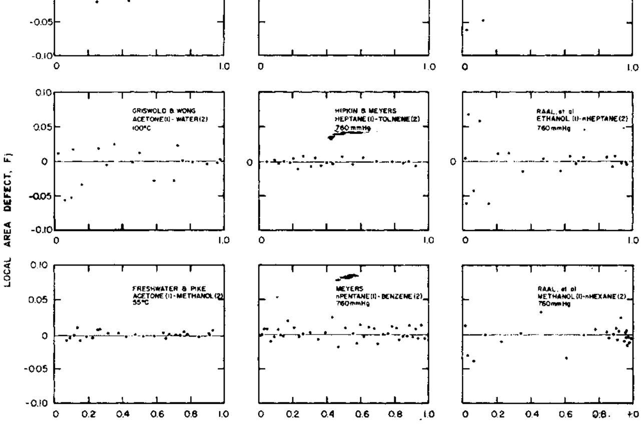

Fig. 2. Local area tests for selected data sets.

TABLE 1. SUMMARY OF CALCULATIONS

Data by	System studied	N	ΣF_j	σ_x, σ_y	σ_T	σ_P	$\sigma_{\Sigma F_j}$	$\Sigma F_j/\sigma_{\Sigma F_j}$	Probability from random sample
Lee and Scheller (1967)	Heptane—propanol at 75°C	20	0.064	0.003	0.2°C	0.2 mm Hg	0.0593	1.08	28%
Griswold and Wong (1952)	Acetone—water at 100°C	21	−0.016	0.002	0.25°C	0.25 mm Hg	0.0941	0.17	86.5%
Freshwater and Pike (1967)	Acetone methanol at 55°C	27	0.0046	5×10^{-4}	0.08°C	0.1 mm Hg	0.022	0.21	83.4%
Ho and Lu (1963)	*n* Hexane—ethanol at 55°C	16	+0.067	0.002	0.15°C	0.20	0.0375	1.79	7.34%
Hipkin and Meyers (1954)	Heptane—toluene at 760 mm Hg	21	0.015	0.002	0.08°C	0.2 mm Hg	0.022	0.682	49.7%
Meyers (1955)	Pentane—benzene at 760 mm Hg	39	0.069	0.002	0.2°C	0.2 mm Hg	0.058	1.2	23%
Katz and Newman (1956)	Ethanol—*n* heptane at 750 mm Hg	19	0.136	0.005	0.4°C	0.2 mm Hg	0.102	1.33	18.4%
Raal, Code and Best (1970)	Ethanol—*n* heptane at 760 mm Hg	22	−0.0288	0.002	0.2°C	0.2 mm Hg	0.048	0.60	54.8%
Raal, Code and Best (1970)	Methanol—*n* hexane at 760 mm Hg	25	−0.065	0.002	0.2°C	0.2 mm Hg	0.056	1.16	24.6%
Granoskaya and Lyubimov (1963)	Lead—silver at 1200°C	11	−0.016				approx. 0.3		

to a systematic error—probably across the whole composition range. However, since the running values of ΣF_j shown in Figure 3 are still of the same order of magnitude as $\sigma_{\Sigma F_j}$ the decision is again borderline.

The data of Granoskaya and Lyubimov (1963) shown in Figure 4 illustrate the dangers involved in considering only the overall area test. Although the data satisfy the overall area test for any reasonable choices of σ_x, σ_y and σ_T, examination of the local areas indicates a clear and quite serious systematic error in the activity coefficients. However, since this error is such that γ_1/γ_2 is too high in one portion of the composition range, and too low in the remainder, the overall area test appears to be satisfied. If only the overall area test had been applied to these data it is likely that they would have been accepted as highly accurate, when it is apparent that they are not!

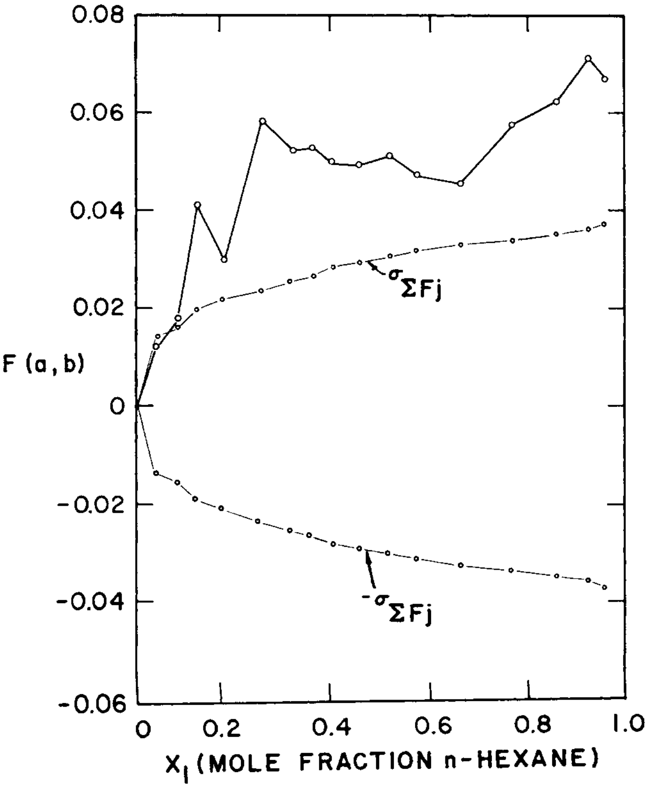

Fig. 3. Running area test for data of Ho and Lu.

The two examples just considered indicate the dangers inherent in using either the local or overall area tests alone. Each test is useful in detecting different kinds of errors: the local area test is best for determining regions of locally severe errors, while the overall test is most useful in detecting low level systematic errors across the whole range of composition. When used in combination the pair of tests is considerably more valuable than either test individually.

If the data of Meyers are plotted as suggested by the integral of Equation (6), the results are as shown in Figure 5. A graphical integration of this curve has been performed and the results presented below (for simplicity the curve has been extrapolated to $x_1 = 0$, and $x_1 = 1$ so that $Q_a = Q_b = 0$)

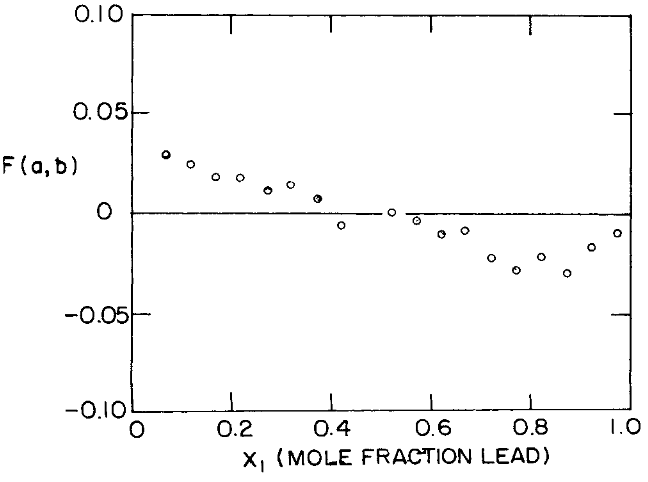

Fig. 4. Local area test for data of Granoskaya and Lyubimov (6).

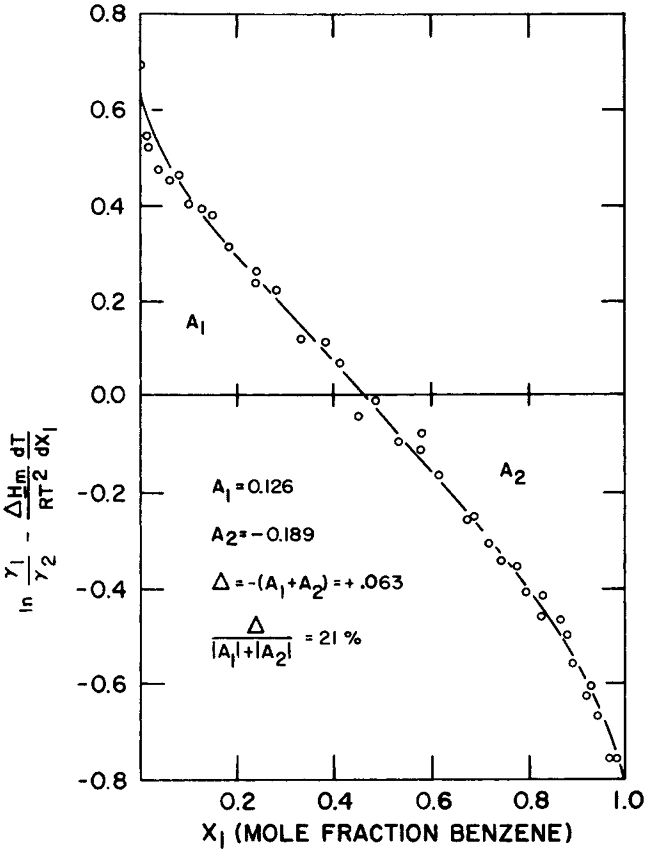

Fig. 5. Overall area test for data of Meyers.

$$
\begin{aligned}
A_1 &= 0.126 \\
A_2 &= -0.189 \\
A_1 + A_2 &= -0.063
\end{aligned}
$$

As required by Equation (6) $A_1 + A_2 \approx -\Sigma F_j$, the discrepancy probably being attributable to the extrapolation, smoothing, and graphical integration performed in Figure 5. The total area defect is 0.063 and is about the same as the expected standard deviation in ΣF_j. Thus there is considerably greater than a 10% probability that this value of ΣF_j is from the proposed random distribution and no basis exists for rejecting the data due to nonsatisfaction of the Gibbs-Duhem equation. This conclusion is reached in spite of the fact that the areas A_1 and A_2 are of considerably different magnitude. These data would probably have been rejected by a standard area test if no statistical guidelines were available to indicate whether or not the area defect was significantly different from zero. This observation is in agreement with the suggestion by Samuels (1972) that the relative fractional area defect is an extremely poor criterion by which to accept or reject experimental data. One may argue that these particular data show an uncomfortably large amount of scatter—and they do—so that great confidence cannot be placed in any individual data point. But there is no statistical evidence to indicate that this scatter is the result of any errors other than randomly distributed measurement errors.

Tao (1964) has also examined these data on the basis of a maximum error propagation equation which is somewhat similar to the statistical error propagation analysis used in this work and that of Ulrichson and Stevenson (1972). Tao concluded that the data were marginally consistent, but only if the heat of mixing term were several times that for the hexane- or heptane-benzene system. Since this appears unlikely, Tao's work infers that these data were unacceptable. The apparent discrepancy between Tao's result and that of this investigation arises as a consequence of using the somewhat vaguely defined maximum error bound as compared to the statistically defined confidence limits of this work. Thus when Tao found that his area defect was slightly greater than his proposed maximum error bands the data would have been rejected. Although this difference in the criteria may not cause serious difficulty when data clearly do not satisfy the Gibbs-Duhem equation, the interpretation of borderline cases is clarified by the use of statistical confidence limits.

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NOTATION

a, b = limits of integration during evaluation of F
C = number of components in system under investigation
P = pressure
R = ideal gas constant
T = temperature
x = liquid phase mol fraction
y = vapor phase mol fraction

Greek Letters

α = ratio of measured to predicted standard deviations
ΔH_m = isothermal enthalpy change on mixing
$\Delta \overline{V}_m$ = isothermal volume change on mixing
σ = standard deviation
γ_i = liquid phase activity coefficient for specie i

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