ν = viscosity
ν_w = viscosity, defined by Equation (2)

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Local Thermodynamic Consistency of Vapor-Liquid Equilibrium Data for Binary and Multicomponent Systems

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The Gibbs-Duhem equation, integrated over specific concentration ranges, is used to determine *local thermodynamic consistency* of vapor-liquid equilibrium data. Several specific applications of the test are given for binary systems, although the method is equally applicable to linear paths in multicomponent systems. The test is particularly useful for evaluating the consistency of incomplete data, that is, data measured over only part of the concentration range.

Since the introductory work of Herington (*1*) and Redlich and Kister (*2*), Prausnitz and Snider (*3*), Van Ness (*4*), and others have extended the applicability of the Gibbs-Duhem equation to test the internal consistency of vapor-liquid equilibrium data for linear paths in multicomponent systems. A test, not restricted to linear paths, was proposed by Li and Lu (*5*) for ternary systems and more recently was extended to multicomponent systems by McDermott and Ellis (*6*). Both the Van Ness and the Li and Lu approaches test for local consistency of the data as well as their overall consistency. A unified consistency test, proposed by Tao (*7*), tests local and overall consistency in binary and multicomponent systems, with consistency or inconsistency being established in terms of the limits of the experimental error of the data. This method, however, becomes relatively insensitive to local inconsistencies at high concentrations when inconsistencies or extrapolation errors at low concentrations are significant.

The purpose of this work is to illustrate the utility, as a precise test for local consistency, of a simple integration of the Gibbs-Duhem equation over a narrow concentration range with the extent of deviation from the null value being an indication of the local inconsistency of the data.

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The most general form of the test equation may be conveniently obtained by integrating by parts the unrestricted Gibbs-Duhem equation as represented by Equation (1):

$$\sum_{i=1}^{n} x_i \, d\ln\gamma_i + (\Delta H/RT^2)\,dT - (\Delta V/RT)\,dP = 0 \quad (1)$$

The resulting equation, given by Van Ness (*8*), is

$$\sum_{i=1}^{n} x_i \ln\gamma_i \Bigg|_{a}^{b} - \sum_{i=1}^{n} \int_a^b \ln\gamma_i \, dx_i + \int_a^b (\Delta H/RT^2)\,dT - \int_a^b (\Delta V/RT)\,dP = 0 \quad (2)$$

APPLICATION OF LOCAL CONSISTENCY TEST

Equation (2) may be used directly to test the consistency of binary data over narrow concentration intervals by computing values of the left side of the equation for $n = 2$ and by plotting the values as a function of x_1. For convenience, the left side of Equation (2) will hereafter be referred to as $f(x)$. The deviation, then, of $f(x)$ from zero is a measure of the inconsistency of the data, just as the magnitude of the area defect is a measure of inconsistency for the case of the area test.

The four examples which follow illustrate the behavior of $f(x)$ for: isobaric data which are reasonably consistent over the entire concentration range, incomplete isobaric data showing local inconsistency, isothermal data showing inconsistency only at high concentrations, and isothermal data which satisfy the area test but show compensating inconsistencies at both high and low concentrations.

The $f(x)$ functions for binary isobaric and isothermal data, represented as $f_P(x)$ and $f_T(x)$, respectively, are readily obtained from Equation (2) and are shown as Equations (3*a*) and (3*b*).

$$f_P(x) = (x_1 \ln\gamma_1 + x_2 \ln\gamma_2)\Bigg|_a^b - \int_a^b \ln\frac{\gamma_1}{\gamma_2}\,dx_1 + \int_a^b (\Delta H/RT^2)\,dT \quad (3a)$$

$$f_T(x) = (x_1 \ln\gamma_1 + x_2 \ln\gamma_2)\Bigg|_a^b - \int_a^b \ln\frac{\gamma_1}{\gamma_2}\,dx_1 - \int_a^b (\Delta V/RT)\,dP \quad (3b)$$

Example 1: *i*-Propanol–Ethylbenzene [Ellis and Froome (*9*)]

The value of $f_P(x)$ for the *i*-propanol–ethylbenzene system was calculated at uniform intervals between $x_1 = 0.1$ and 0.9 (actual data ranged from $x_1 = 0.067$ to 0.942) from smoothed values of the vapor-liquid equilibrium data at 760 mm. Hg. The heat of mixing contribution was estimated from the data of Mrazek and Van Ness (*10*). Uniform intervals of $\Delta x = 0.1$ were used in each of the four examples considered, and integration was accomplished by means of the integrated Newton interpolation formulae.

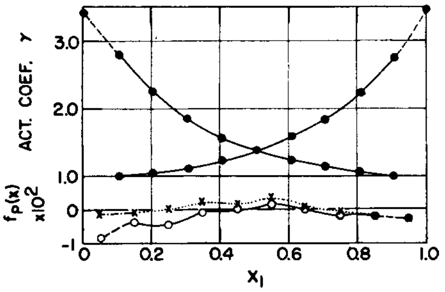

Fig. 1. *i*-Propanol–ethylbenzene, 760 mm. Hg (*9*).

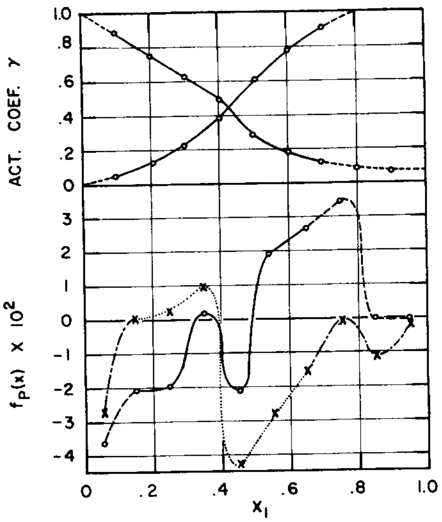

Fig. 2. Nitric acid-water, 760 mm. Hg (*12*).

Figure 1 is a plot of the smoothed activity coefficient data and shows the fluctuation of $f_P(x)$ as a function of x_1. The dotted line represents $f_P(x)$ minus the heat of mixing term. It is apparent that $f_P(x)$ fluctuates only slightly about $f_P(x) = 0$ in both cases, indicating reasonable local consistency. It is also apparent that the heat of mixing contribution to $f_P(x)$ is small. Application of Equation (3*a*) over the entire concentration range, based on extrapolations of the alpha function (*11*), where, $\alpha_i = \ln\gamma_i/(1 - x_i)^2$, to $x_1 = 0$ and 1.0, indicates overall consistency with an area defect of less than 0.5% of the total area. Extrapolations and corresponding $f_P(x)$ values are shown as dashed lines.

Example 2: Nitric Acid-Water [Ellis and Thwaites (*12*)]

Experimental isobaric data between $x_1 = 0.061$ and 0.719 were smoothed and $f_P(x)$ calculated as before with the heat of mixing term estimated from data given in Perry's Handbook (*13*). These results are represented in Figure 2 with the dotted line again representing $f_P(x)$ minus the heat of mixing term. Extrapolations of the activity coefficients to dilute concentrations with the alpha function are obviously questionable. It is apparent from the $f_P(x)$ plot that marked inconsistencies exist in the data and that the heat of mixing term is rather significant.

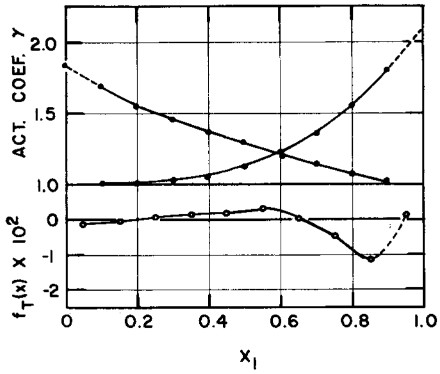

Fig. 3. Lead-silver, 1,000°K. (*14*).

Example 3: Lead-Silver [Aldred and Pratt (*14*)]

Values of $f_T(x)$ were calculated for the lead-silver system at 1,000°K. from smoothed isothermal data reported between $x_1 = 0.1$ and 0.9. The volume change of mixing term was neglected with little effect on $f_T(x)$. Activity coefficients and $f_T(x)$ values for this system are plotted in Figure 3. The area test applied to these data indicates consistency trouble with an area defect of 13%. However, it is apparent from the $f_T(x)$ plot that the difficulty is localized in about the upper fourth of the concentration range while the lower three fourths show good local consistency.

Example 4: Lead-Silver [Granovskaya and Lyubimov (*15*)]

Smoothed isothermal data were again used to calculate $f_T(x)$ values between $x_1 = 0.1$ and 0.9. The results, along with extrapolations based on the alpha function, are represented in Figure 4. These results point out inconsistencies at both ends of the concentration scale and particularly illustrate local consistency problems associated with extrapolations. Based on the authors' extrapolations, the area test gives an area defect of only 3%, deceptively implying relatively good overall consistency.

To illustrate the effect of cumulative integration, the function $F(x)$ is defined to represent the value of Equation (2) with the lower limit of integration being held at its initial value (zero in both examples considered). Figure 5 represents $F_T(x)$ as a function of x_1 (upper limit) for the two isothermal systems. The relative insensitivity of the cumulative integration to local inconsistency is apparent for the case of example 4. Only in the case of consistency in the low concentration regions does the cumulative integration satisfactorily indicate local inconsistency as illustrated by example 3.

SUMMARY

In summary, it is apparent that one disadvantage of the local consistency test illustrated here is that the extent of the inconsistency measured is relative with no absolute scale of comparison. Also, it is not possible, in most cases, to determine which data are responsible for the inconsistency, that is, whether of component 1 or 2.

The most significant advantages of the test appear to be: its suitability to measure local consistency of data (with an integration procedure) which is unmasked by inconsistencies in other parts of the concentration range, and its applicability to test the consistency of incomplete sets of data such as those of nitric acid-water system of example 2 without including the uncertainties of extrapolation errors.

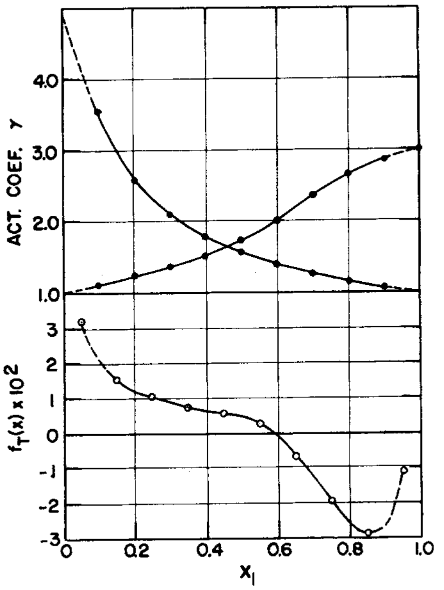

Fig. 4. Lead-silver, 1,200°K. (*15*).

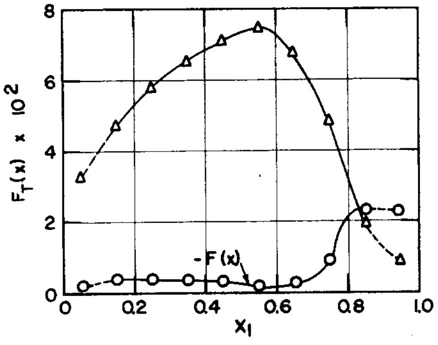

Fig. 5. Local consistency based on integration of Equation (4*b*) with lower limit at $x_I = 0$. ○ Lead-silver (*14*), example 3. △ Lead-silver (*15*), example 4.

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NOTATION

a,b = subscripts denoting limits of integration
ΔH = enthalpy change of mixing at constant T and P per mole of solution formed
n = number of components
P = pressure
R = gas constant
T = absolute temperature
ΔV = volume change of mixing at constant T and P per mole of solutions formed
x_1 = mole fraction of the first mentioned component
x_i = mole fraction of component i
γ_i = activity coefficient of component i

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