through void space in packed bed, kg.-cal./(sq. m.)(hr.)

q = purely radial heat flow in annular packed bed, kg.-cal./(hr.)

q^* = heat loss from test section of annular packed bed, kg.-cal./(hr.)

q' = purely radial heat flow in annular packed bed for blank test, kg.-cal./(hr.)

q_o = purely radial heat flow in annular packed bed with stationary fluid, kg.-cal./(hr.)

t_f = mean temperature of fluid in void space, °C.

t_v = mean temperature of fluid in void space nearest to wall surface, °C.

Δt_o = apparent temperature difference in annular packed bed, °C.

$\Delta t_o'$ = apparent temperature difference in annular packed bed for blank test, °C.

Δt_o^* = apparent temperature difference in annular packed bed with stationary fluid, °C.

Δt_1 = apparent temperature difference on inner tube surface of annular packed bed, °C.

Δt_2 = apparent temperature difference on outer tube surface of annular packed bed, °C.

V = rate of vapor condensation in annular packed bed, kg./(hr.)

V_o = rate of vapor condensation in annular packed bed with stationary flund, kg./(hr.)

V' = rate of vapor condensation in annular packed bed for blank test, kg./(hr.)

Greek letters

α = (mass velocity of fluid flowing in direction of heat or mass transfer)/(mass velocity of fluid based on sectional area of empty tube in direction of fluid flowing)

α_w = above value near wall surface in packed bed

β = (effective length between centers of two neighboring solids in direction of heat flow)/(average diameter of solid)

γ = latent heat of vapor condensation, kg.-cal./kg.

ϵ = void fraction of packed bed

μ = viscosity of fluid, kg./(m.)(hr.)

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Thermodynamic Consistency of Binary Liquid-Vapor Equilibrium Data When One Component Is Above Its Critical Temperature

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Methods are developed for testing binary system phase-equilibrium data for thermodynamic consistency when the more volatile component is above its critical temperature. The isothermal case with varying pressure and the isobaric case with varying temperature are considered individually. The rigorous form of the Duhem equation is employed rather than the simplified one, which for binary systems is inconsistent with the phase rule. Although derived for the specific case given in the title, the relationships developed are applicable to all conditions of binary systems. Sample calculations illustrating the methods are included.

As the design procedures originally applied to petroleum plant distillation problems have spread to the chemical and petrochemical fields, there has been an increasing need to use laboratory-obtained phase-equilibrium data. With this has developed the need for establishing the thermodynamic consistency of such information. Considerable attention has been given to this subject in the literature (*1*, *4* to *8*, *13*, *17*).

All methods published for making the necessary thermodynamic tests for reliability are based on some form of the Duhem equation. Some authors (*7*, *17*) have allowed for the fact that a binary system cannot change in composition when both temperature and pressure remain constant; others have not. A few have included a correction for the nonideality of the vapor phase above the solution. Most of the methods

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have been developed for testing sets of isobaric data, but some pertain to isothermal data.

None of the published articles have considered the case where a stable liquid phase does not exist over the whole range of composition from one extreme of pure component *A* to the other of pure component *B*. This arises when the mixture is at a temperature above the critical temperature of the light component. Examples of data reported where one component is above its t_c are ethane-propylene (*9, 10*), hydrogen-methane (*3, 15*), methane-propane (*12*), and the many systems included in the text by Ruhemann (*14*) on the separation of gases.

The Duhem equation in the approximate form

$$x_1\, d\ln \gamma_1 + x_2\, d\ln \gamma_2 = 0 \quad (\text{constant } \pi,\ t) \qquad (1)$$

is commonly associated with this problem of testing thermodynamic consistency. For the purpose of testing a set of experimental data the activity coefficients of each component are plotted vs. composition. The areas under each of the two lines are then examined. According to this test the two areas are equal if the data are consistent. A similar diagram for the case described in the preceding paragraph is given in Figure 1. In actuality, when both activity coefficients are based on the components in their pure state, as is conventionally the case in drawing these diagrams, Figure 1 cannot really be obtained. Because the lighter component is above its critical point, no vapor-pressure curve is available to calculate a γ. Unless the temperature is only slightly above t_c, any extrapolation of the vapor-pressure curve would be too inaccurate to reach a conclusion about thermodynamic consistency. Except for the work of Ibl and Dodge (*7*), all the published methods for testing the consistency of the data depend on the use of activity coefficients and vapor pressures.

It was the objective of the present work to develop methods for testing both isothermal and isobaric data for binary systems: that are not dependent on vapor pressures and activity coefficients; that are not restricted to a vapor phase that is ideal; that do not assume that the volume of the liquid is negligible; that do not necessitate drawing a tangent to temperature–composition or pressure–composition lines, with resulting compromises in accuracy; and that do not assume that the composition of the liquid for a binary system can be varied at constant temperature and pressure.

Aside from the practical difficulty of computing activity coefficients referred to the pure liquid as a standard state when the temperature is above the component's critical value, γ's have been avoided for another reason. In many cases, particularly where extrapolating data or combining various sets of data is not involved, use of activity coefficients is not only unnecessary but complicates the procedure.

It should be emphasized that although the methods of testing data developed below are for the purpose of handling problems where the more volatile component is above its critical, such methods have general application at all temperatures.

THE CONSTANT-TEMPERATURE CASE

As a starting point for the present study Equation (2), which is developed by Ibl and Dodge (*7*) as their Equation (7), is selected:

$$x_1\, d\ln f_1 + x_2\, d\ln f_2 = \frac{v^L}{RT}\, d\pi = \frac{v^L \pi}{RT}\, d\ln\pi \qquad (2)$$

When one assumes that the Lewis and Randall fugacity rule applies to the vapor phase,

$$f_i = y_i f_i^* = y_i \pi \nu_{i\pi} = K_i x_i \pi \nu_{i\pi} \qquad (3)$$

First one should substitute $y_i \pi_i \nu_{i\pi}$ for f_i and let

$$Z^L \equiv \frac{v^L \pi}{RT}$$

$$x_1 d\ln\, (y_1\, \pi \nu_{1\pi}) + x_2 d\ln\, (y_2 \pi \nu_{2\pi}) = Z^L\, d\ln \pi \qquad (4)$$

Alternately, in terms of *K* constants one should replace f_i with $K_i x_i \pi \nu_{i\pi}$ and simplify to yield

$$x_1 d\ln\, (K_1 \pi \nu_{1\pi}) + x_2 d\ln\, (K_2\, \pi \nu_{2\pi}) = Z^L\, d\ln\pi \qquad (5)$$

The two principal expressions obtained so far, Equations (4) and (5), make use of the fugacity coefficient to allow for the nonideality of the vapor phase. If it is more convenient to work with compressibility factors instead of $\nu_{i\pi}$, the modified Duhem equation is developed as follows:

$$f_i = \pi\, y_i\, e^{\left(\int_0^\pi \frac{\overline{v_i{}^g}}{RT} d\pi - \int_0^\pi \frac{d\pi}{\pi}\right)} \qquad (6)$$

$$d\ln f_i = d\ln\, (\pi\, y_i) + \left(\frac{\pi \overline{v}_i{}^g}{RT} - 1 \right) d\ln\, \pi \qquad (7)$$

and

$$Z_i{}^g \equiv \frac{\pi \overline{v}_i{}^g}{RT}$$

Inasmuch as it is assumed that the Lewis and Randall rule applies to the vapor, one can replace $\overline{v}_1{}^g$ with $v_1{}^g$, the molar volume of the pure component. However for component 2, which is in a supercooled state as a gas, the value of $\overline{v}_2{}^g$ would have to be found by extrapolation into an unstable region. Instead $\overline{v}_2{}^g$ is introduced as follows.

Because $v^g = y_1\, \overline{v}_1{}^g + y_2\, \overline{v}_2{}^g$, when the partial molal values are replaced,

$$\overline{v}_2{}^g = \frac{v^g - y_1 \overline{v}_1{}^g}{y_2} \cong \frac{v^g - y_1 v_1{}^g}{y_2}$$

If now y_i/K_i is substituted for x_i, the following expression is finally obtained from (2):

$$x_1\, d\ln K_1 + x_2\, d\ln K_2 = \left[Z^L + Z_1{}^g\, y_1 \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{Z^g}{K_2} \right] d\ln \pi \qquad (8)$$

All the quantities in this equation can be evaluated from the experimental equilibrium data or from data on the pure components without extrapolation into metastable regions.

When one integrates between the limits where $x_1 = 0$ and some maximum concentration $x_1 = x_b$ and between the corresponding limits for the *K*'s,

$$\int_{K_1(0)}^{K_1(x_b)} x_1\, d\ln K_1 + \int_{K_2(1)}^{K_2(1-x_b)} x_2\, d\ln K_2 = \int_{\pi(0)}^{\pi(x_b)} \left[Z^L + Z_1{}^g\, y_1 \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{Z^g}{K_2} \right] d\ln\pi \qquad (9)$$

where $K_1(x_1)$ is regarded as a function of x_1, $K_2(x_2)$ as a function of x_2, and $\pi(x_1)$ as a function of x_1.

Where experimental volumes are available, the values of *Z* may be found directly; otherwise they are obtained from generalized charts.

The three terms in Equation (9), or the integrated forms of Equation (4) or (5), represent areas designated from left to right as A_1, A_2, and A_3. In the commonly found simplified form of the Duhem equation, Equation (1), as noted previously $A_3 = 0$ and $A_1 = A_2$ for consistent data. Examination of Equations (4), (5), and (9) will show that with a sufficient change in pres-

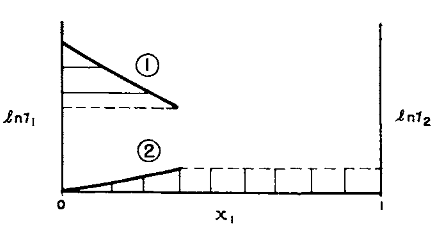

Fig. 1. Activity-coefficient—composition diagram (one component above the critical temperature).

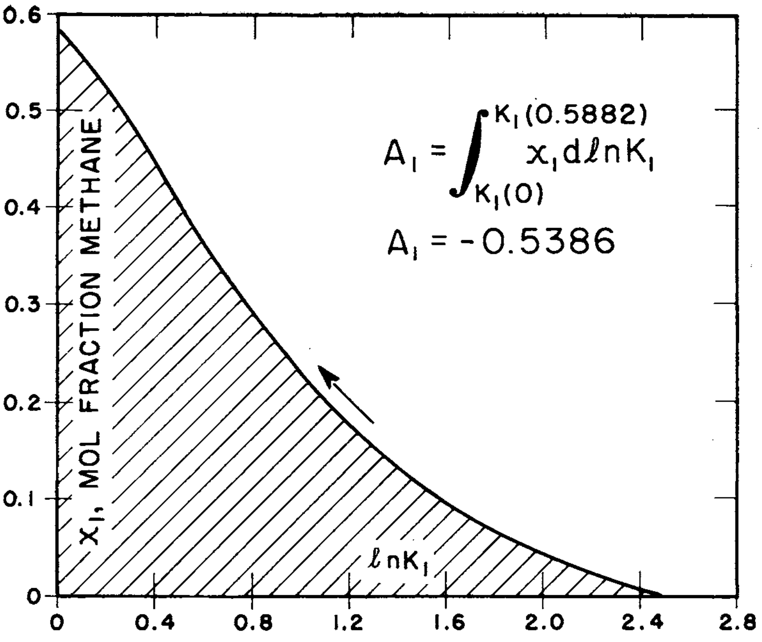

Fig. 2. Graphical integration for term 1 of Equation (9).

sure A_3 may not even be close to zero for isothermal data. In the sample calculations included with this paper, for instance, the following areas were obtained:

Equation (9)

$$\left.\begin{array}{l} A_1 = -0.5386 \\ A_2 = -0.3079 \end{array}\right\} -0.8465$$
$$A_3 = -0.8612$$

Equation (4)

$$\left.\begin{array}{l} A_1 = 0.3670 \\ A_2 = -0.0828 \end{array}\right\} 0.2842$$
$$A_3 = 0.2927$$

for the system methane-propane (*12, 16*). The areas are different when calculated according to Equation (9) on the one hand and Equation (4) on the other because in the former all the vapor-phase deviations from Dalton's law are included in A_3, whereas according to Equation (4) they are included in A_1 and A_2. In the latter case A_3 results only from the finite liquid volume.

In another application of Equation (9) for the ethane-propylene system, with the data of McKay (*10*) used, the *A*'s were as follows at 10°F.:

$$\left.\begin{array}{l} A_1 = 0.2204 \\ A_2 = 0.2867 \end{array}\right\} 0.5071$$
$$A_3 = 0.5112$$

The corresponding change in pressure was from 58 to 255 lb./sq. in. abs. For the same system Lu *et al.* (*9*) reported data at 14°F. which yielded the following areas:

$$\left.\begin{array}{l} A_1 = 0.274 \\ A_2 = 0.404 \end{array}\right\} 0.678$$
$$A_3 = 0.431$$

In this case the pressure change was from 62 to 270 lb./sq. in. abs. (The degree of consistency of each of these sets of data for the ethane-propylene system will be discussed later in this paper.)

THE CONSTANT-PRESSURE CASE

Ibl and Dodge (*7*), using the same basic principles represented by Equation (2), given under the constant-temperature case, plus the fact that

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{\pi,\, x_i} = \frac{H_i^{*\prime} - \overline{H}_i^{L}}{RT^2} \qquad (10)$$

show that

$$\frac{d\ln f_1}{d\ln x_1} = \frac{d\ln f_2}{d\ln x_2} + \frac{\Delta H}{RT^2}\frac{dT}{dx_1}$$

at constant pressure (11)

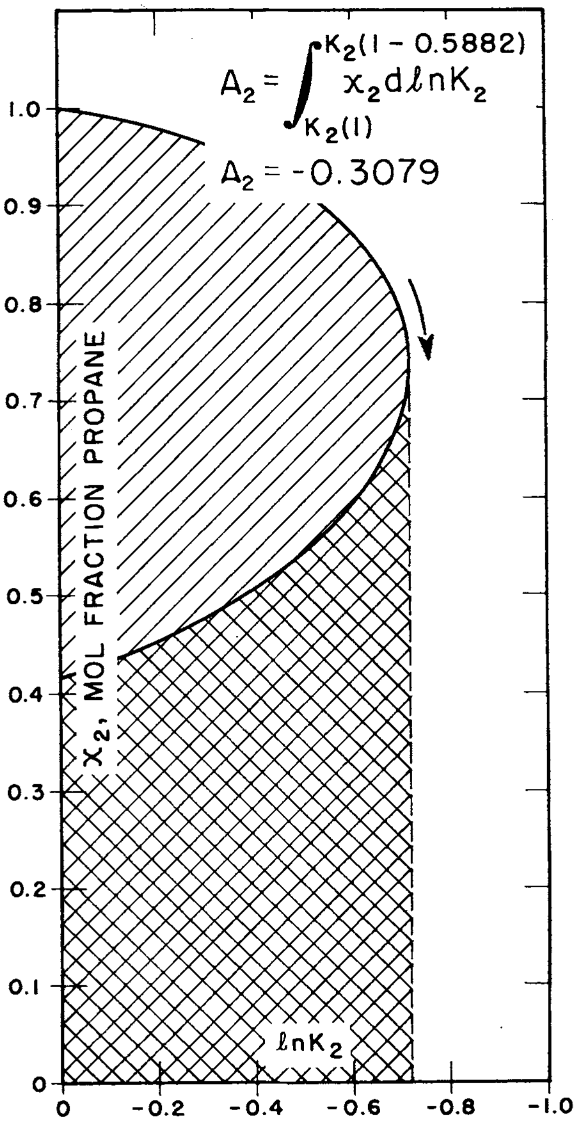

Fig. 3. Graphical integration for term 2 of Equation (9).

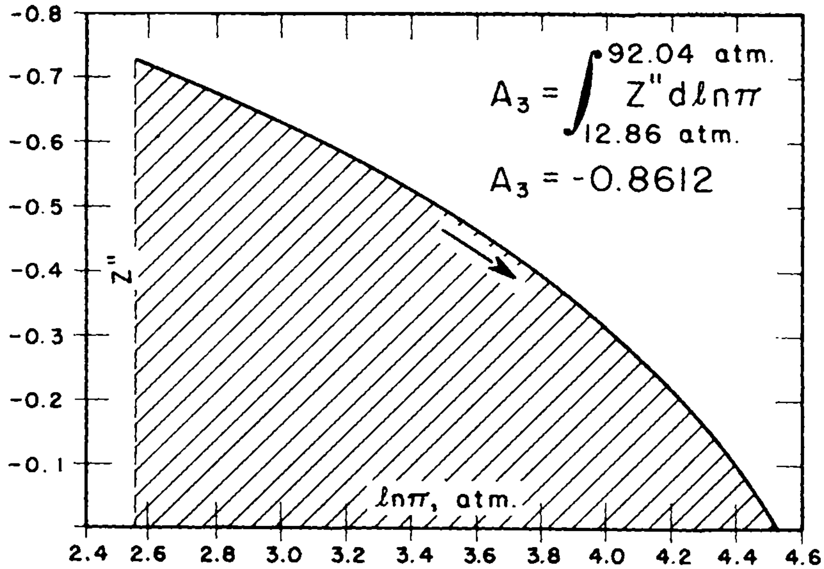

Fig. 4. Graphical integration for term 3 of Equation (9).

$$\Delta H = x_1 H_1^{\circ g} + x_2 H_2^{\circ g} - x_1 \overline{H}_1^L - x_2 \overline{H}_2^L$$

which is the molal ideal heat of vaporization for the solution. It equals the heat of mixing of the pure liquids plus the heat of vaporization of the pure liquids. Replacing $d\ln f_i$ with $d\ln (K_i x_i \pi \nu_{i\pi})$ as in (3), and simplifying, yields

$$x_1\, d\ln K_1 \nu_1 + x_2\, d\ln K_2\nu_2 = \frac{\Delta H}{RT^2} dT \quad (12)$$

The integral form of Equation (12) again represents three areas to be designated A_1, A_2, and A_3, as before.

There are several methods of obtaining ΔH. Ibl and Dodge suggest that if the heat of mixing is not available it can be neglected and ΔH can be assumed equal to the ideal heat of vaporization. However the heat of mixing can be obtained from the heats of solution at infinite dilution when they are available (*11*); that is, $\Delta H_{mix} = x_1 x_2 (L_1{}^\circ x_2 + L_2{}^\circ x_1)$.

If more than one set of isobaric data is available, plots of the partial pressure of each component, $y\,\pi$, vs. $1/T$ at constant compositions will enable the partial molal heats of solution to be obtained. The partial heats of solution are then combined to obtain ΔH. This procedure is particularly useful if the temperature exceeds the t_c of the light component.

In order to point out the size of the terms in Equation (12) that may be expected when the temperature varies, the following areas were measured for the reported atmospheric liquid-vapor equilibria for methanol-water (*18*):

$$\text{If } A_1 + A_2 = A_3,$$
$$\left.\begin{aligned} A_1 &= 0.614 \\ A_2 &= 0.726 \end{aligned}\right\} 1.340$$
$$A_3 = 1.325$$

This should make it clear that one does not have to be working above the critical temperature before the third area becomes important.

SIGNIFICANCE OF THE RESULTS OF THE THERMODYNAMIC-CONSISTENCY TEST

To some degree a judgment of the thermodynamic consistency of the data tested can be made by an examination of the unbalance in the equation relating the areas; that is, $A_1 + A_2 = A_3$. Then one might ask how serious the various amounts of unbalance are. One answer may be found by the use of the K_1 values or the observed y_1 values in Equation (4), (5), (9), or (12) and by the calculation of the K_2's or y_2's to make the equation balance. Process requirements can then be evaluated with both sets of K's and the difference in the two designs (number of trays, reboiler duty, for example) examined.

By a comparison of the degree of unbalance obtained from testing the consistency of each of two or more sets of experimental data for the same system, one set may be accepted in preference to the others. In the section on constant temperature the results were given from testing the data of two different investigators of the ethane-propylene system. The sum of areas $A_1 + A_2$ for the data of McKay *et al.* (*10*) was 0.5071, which nearly equals an A_3 of 0.5112. On the other hand the corresponding values for the data of Lu *et al.* (9) were 0.678 and 0.431, respectively. It is obvious that the data of McKay *et al.* should be selected. This illustrates one of the most important uses of thermodynamic-consistency testing.

The unbalance in the areas may result from errors in measurement of compositions, temperatures, or pressures or from the slight inaccuracy of the Lewis fugacity rule and the corollary assumption of additivity of vapor volumes. Other methods of answering this question may lead to a sequel to this paper.

ILLUSTRATION OF THE TESTING OF ISOTHERMAL DATA

The experimental data (Table 1) of Reamer *et al.* (*12, 16*) for the methane-propane system at 100°F., where methane is above its critical temperature, are to be tested for thermodynamic consistency. The data for only the lowest, an interim, and the highest pressures are shown, inasmuch as the reference is readily available. These data, plus the corresponding calculated data in Table 2, permit the limits of the various expressions which are graphically integrated to be understood. Figures 2, 3, and 4 for the solution based on the volumes and compressibility factors [Equation (9)] present areas A_1, A_2, and A_3, respectively. A similar group of three plots for the solution based on fugacity coefficients [Equation (4)], although not included here, was also plotted to obtain these areas. These two equations, along with the numerical values of the areas, are

$$\underset{(-0.5386)\;+}{\int_{K_1(0)}^{K_1(0.5882)} x_1\, d\ln K_1} + \underset{(-0.3079)\;\cong}{\int_{K_2(1)}^{K_2(1-0.5882)} x_2\, d\ln K_2} = \underset{(-0.8612)}{\int_{12.86 \text{ atm.}}^{92.04 \text{ atm.}} Z''\, d\ln \pi}$$

and

$$\underset{(0.3670)\;+}{\int_{y_1 \pi\nu_{1\pi} \text{ at } x_1 = 0}^{y_1 \pi\nu_{1\pi} \text{ at } x_1 = 0.5882} x_1\, d\ln(y_1\, \pi \nu_{1\pi})} + \underset{(-0.0828)\;\cong}{\int_{y_2 \pi\nu_{2\pi} \text{ at } x_1 = 0}^{y_2 \pi\nu_{2\pi} \text{ at } x_1 = 0.5882} x_2\, d\ln(y_2\, \pi \nu_{2\pi})} = \underset{(0.2927)}{\int_{12.86 \text{ atm.}}^{92.04 \text{ atm.}} Z^L\, d\ln \pi}$$

It will be observed that on each of the figures the direction of the integration is designated. When three areas are handled simultaneously, the signs must be made consistent throughout the calculations, requiring greater care than normally. To aid in obtaining this consistency it is helpful to make the lower limits of all three integrals correspond to the lower limit in x_1, even though this may change the customary direction of integration. When integration is from a higher value of the differential variable to a lower one, the sign of the area is reversed.

LIMITATIONS OF THE METHODS PRESENTED

Equations (4), (5), and (8) for

TABLE 1. METHANE-PROPANE EQUILIBRIUM DATA (*12, 16*)

Temperature = 100°F.

Pressure, atm.	x_1	y_1	v^g, cu. ft./lb.-mole	v^L, cu. ft./lb.-mole	v_1^g, cu. ft./lb.-mole
12.86	0	0	24.54	1.494	31.28
47.62	0.2019	0.6073	6.30	1.448	7.96
92.04	0.5882	0.5882	2.083	2.083	3.914

Component 1 = methane.

TABLE 2. METHANE-PROPANE EQUILIBRIUM DATA (12)—APPLICATION OF EQUATIONS

Pressure, atm.	K_1	K_2	Z^L	Z''	$\nu_{1\pi}$	$\nu_{2\pi}$	$\ln(y_1\pi\nu_{1\pi})$	$\ln(y_2\pi\nu_{2\pi})$	$\ln\pi$
12.86	—	1.0	0.0471	—0.7260	0.987	0.823	—	2.359	2.554
47.62	3.01	0.4920	0.1689	—0.3654	0.948	0.435	3.311	2.096	3.863
92.04	1.0	—	0.4698	0	0.889	0.250	3.874	2.249	4.522

testing constant-temperature data have been developed with the aid of the Lewis and Randall rule, which assumes an ideal solution for the vapor phase. When the critical pressure of the mixture is approached, such an assumption cannot be expected to hold. If no partial-volume data are available, as is usually the case, a generalized correlation for compressibility factors must be used when Equation (8) is applied. Similarly, generalized fugacity-coefficient charts are required for Equations (4) and (5).

When one tests isobaric data with the aid of Equation (12), results are not limited by the assumption of an ideal solution for the vapor phase. However the use of a generalized chart for the fugacity coefficient is again necessary.

The accuracy of the final result depends upon how the generalized fugacity correlations fit the system under study.

CONCLUSIONS

Methods have been presented for testing the thermodynamic consistency of data when the more volatile component is above its critical temperature; these methods are free of many of the restrictions and disadvantages found in procedures published earlier.

It has been demonstrated that the areas corresponding to the two terms of the Gibbs-Duhem equation in its commonly used approximate form are frequently not equal, even when the data are thermodynamically consistent. The third term, or so-called "correction term," may be larger than one of the "main" terms, and for consistent data it approximates the algebraic sum of the first two terms.

ACKNOWLEDGMENT

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NOTATION

f = fugacity, atm.

f^* = fugacity of the pure component at the same temperature and pressure as that of the solution, atm.

H = molal enthalpy, B.t.u./lb.-mole

$\overline{H}$ = partial molal enthalpy, B.t.u./lb.-mole

H^{*g} = molar enthalpy of the ideal gas, B.t.u./lb.-mole

H^{oL} = molar enthalpy of the pure liquid, B.t.u./lb.-mole

ΔH = ideal molal heat of vaporization of the solution, B.t.u./lb.-mole

ΔH_{mix} = molal heat of mixing, B.t.u./lb.-mole of solution

K = liquid-vapor equilibrium constant $\equiv y/x$

L_i^o = heat absorbed on solution at infinite dilution of one mole of component i as a liquid $\equiv \overline{H}_i^L - H_i^{oL}$

R = gas constant = 0.730 atm. cu. ft./lb.-mole °R., or 1.986 B.t.u./lb.-mole °R.

T = absolute temperature, °R.

t = temperature, °F.

v = volume per mole, cu. ft./lb.-mole

$\overline{v}$ = partial molal volume, cu. ft./lb.-mole

x = mole fraction in liquid phase

y = mole fraction in vapor phase

Z = compressibility factor = $(\pi v)/(RT)$

Z'' $\equiv -Z^L + Z_1^g y_1(1/K_2 - 1/K_1) - Z^g/K_2$

γ = liquid-phase activity coefficient

ν = fugacity coefficient (used here exclusively for the vapor phase of a pure component at the temperature and pressure of the system)

π = total pressure of the system, atm.

Subscripts

b = maximum observed concentration in the liquid of more volatile component

c = critical point

i = any component of a liquid or vapor solution

π = total pressure of the system

1, 2 = components of a binary solution

Superscripts

g = gas phase

L = liquid phase

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