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A Thermodynamic Equation Relating Equilibrium Vapor-Liquid Compositions and Enthalpy Differences in Isobaric Multicomponent Systems

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A rigorous and simple thermodynamic equation relating equilibrium vapor-liquid compositions and the phase enthalpy differences for a binary, isobaric system is extended to multicomponent systems. An analysis is made to indicate the potential applications of computing the latent heat of vaporization directly from the isobaric vapor-liquid equilibrum data and testing the consistency of phase composition and enthalpy data.

Enthalpy information of multicomponent systems is important to the design of distillation equipment, especially for the high pressure, multicomponent systems of which experimental enthalpy studies are costly and combinations of components are numerous. Studies have been made to estimate enthalpy from P-V-T data or equations of state. Papadopoulos, Pigford, and Friend (*1*), and Edmister and Canjar (*3*) used the partial enthalpy calculated from the Benedict-Webb-Rubin equation of state (*2*). Stiehl, Hobson, and Weber (*18*) pointed out the questionable reliability of the B-W-R equation in the liquid phase region; they then suggested the use of differential heat of condensation to estimate the enthalpy of saturated liquid from that of the saturated vapor. Bahlke and Kay (*1*) showed a rigorous method, and Edmister (*4*) proposed an approximate method to calculate the integral heat of condensation.

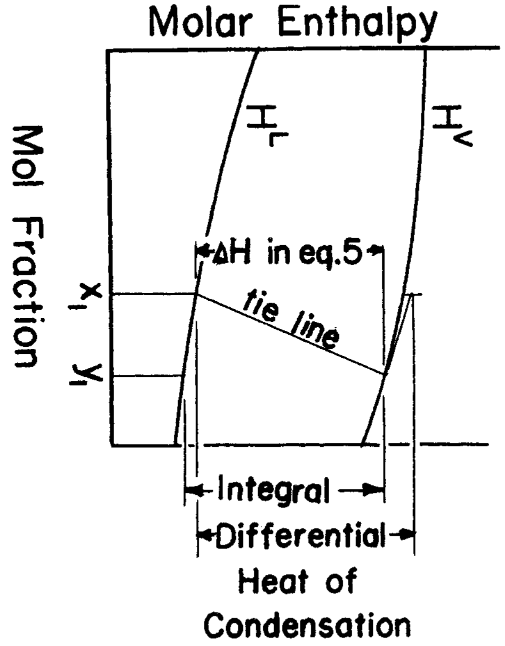

Fig. 1. Various enthalpy differences.

During their search of methods to calculate the vapor composition from the vapor pressure data, Ljunglin and van Ness (*12*, *20*) showed an interesting equation for binary systems to relate the phase enthalpy difference (Figure 1) and x-y-T data. This paper extends their equation to the multicomponent systems, examines the limit forms, and discusses the potential applications of estimating the latent heat directly from x-y-T data, checking the consistency between the phase composition and enthalpy, and estimating the vaporization ratio of a component with several trace components.

THEORY

The unrestricted form of Gibbs-Duhem equation was obtained by Ibl and Dodge for a binary (*9*) and later extended by van Ness (*20*) to a completely unrestricted form for multicomponent systems. For a single phase system, Equations (1) and (2) describe the thermodynamic relationship between variables in a liquid and a vapor mixture respectively:

$$\sum_i x_i \, d\ln f_i^L = \frac{H^* - H^L}{RT^2} dT + \frac{V^L}{RT} dP \qquad (1)$$

$$\sum_i y_i \, d\ln f_i^V = \frac{H^* - H^V}{RT^2} dT + \frac{V^V}{RT} dP \qquad (2)$$

The usual use of Equation (1) in the vapor-liquid equilibrium studies involves either the substitution of f_i^L for f_i^V by virtue of phase equilibrium, or the subtraction of Equation (3), which describes standard states of various components, to give Equation (4) as the most familiar form (*20*).

$$\sum_i x_i \, [d\ln f_i^o] = \sum_i x_i \left[\frac{H^* - H_i^{oL}}{RT^2} \right] dT + \sum_i x_i \left[\frac{V^{oL}}{RT} \right] dP \qquad (3)$$

$$\sum_i x_i \, d\ln \gamma_i = -\frac{H_M{}^L}{RT^2} dT + \frac{V_M{}^L}{RT} dP \qquad (4)$$

When a system has a liquid and a vapor phase in equilibrium, f_i^L equals f_i^V for any component i. The fugacity f_i and P (for isothermal data) or T (for isobaric data) would be respective hypersurfaces in a composition space such as those shown in Figure 2. Therefore, the derivatives of f_i^L and of f_i^V would be identical. Hence, if the coexisting equilibrium phases are described by Equations (1) and (2), the difference should be (5) for an isobaric system.

$$\sum_i (x_i - y_i) \, d\ln f_i^V = \frac{\Delta H - \Delta H^*}{RT^2} dT \qquad (5)$$

Equation (5) is the proposed equation which rigorously describes the molar enthalpy difference between two equilibrium phases and the x-y-T data since the vapor phase fugacities are functions of known P, T and y. The existence of ΔH^* is due to the difference between the compositions of two phases and $\Delta H^* = H^*(y_1, y_2 ---) - H^*(x_1, x_2 ---)$. H^* of any ideal gas mixture of known composition can be calculated from H^* of components. In turn, H^* of a component can be calculated from molal heat capacities in the literature (*8, 10, 11, 16*). Therefore, ΔH can be computed from the x-y data and the temperature profile if the vapor phase fugacity can be obtained such as by using the equations of state or the experimental P-V-T data.

The main advantages of using Equation (5) in estimating the latent heats are by having only constrained ordinary derivatives and simplicity for multicomponent systems. For example, the rigorous equation used by Stiehl et al. (*18*) needs information on saturated liquid densities, several sets of equilibrium data at pressure levels in the neighborhood of the pressure of interest to evaluate a partial derivative, and P-V-T data of vapor mixtures. Equation (5) requires only the last item of information.

LIMIT FORMS

When the phase composition, or the condition, changes to approach a physical limit, Equation (5) may approach some simple form. These forms not only represent the working equations at those limits but also shed some insight to the proposed equation. The three limiting cases are a mixture composition approaching a pure component, a mixture approaching its azeotrope composition, and a mixture at the critical point.

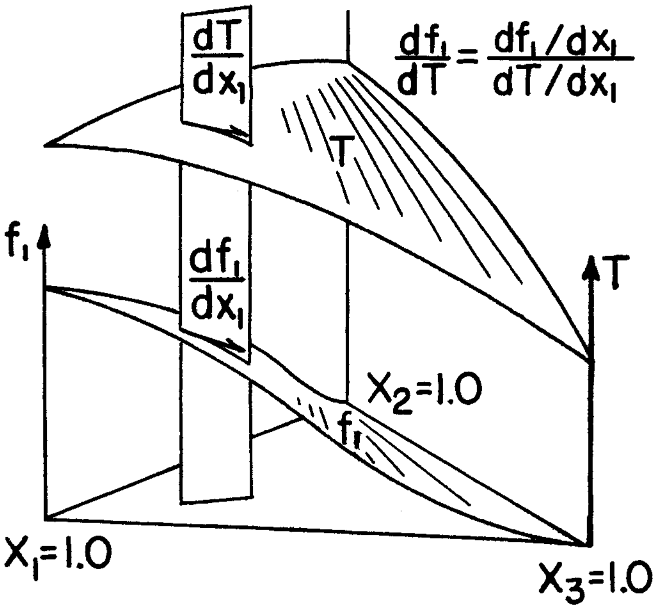

Fig. 2. Fugacity and temperature surfaces of a ternary system.

Composition Approaching a Pure Component

As the mixture composition approaches that of a pure component j, the mole fractions and fugacity of j in both phases will approach a finite f_j^o while those of non-j approach zero. If we let $(x_i - y_i)d \ln f_i^V = [(x_i - y_i)/f_i^V]d\, f_i^V$, the limits of terms on the left side of Equation (5) becomes:

$$\lim_{x_j \to 1.0} [(x_j - y_j)/f_j^V]d\, f_i^V = [(1-1)/f_j^o]d\, f_j^V = [0]d\, f_j^V$$

and

$$\lim_{x_i \to 0.0} [(x_i - y_i)/f_i^V]d\, f_i^V = [(0-0)/0]d\, f_i^V$$
$$= [d(x_i - y_i)/d\, f_i^V]d\, f_i^V = d(x_i - y_i)$$

Therefore, after combining with

$$\sum_{i \neq j} d(x_i - y_i) = -d(x_j - y_j)$$

Equation (5) becomes Equation (6) or its equivalent form (6*a*). They are of the same forms of the binary systems derived by van Ness (*20*). Thus

$$d(x_j - y_j) = -\frac{\Delta H}{RT^2} dT \qquad (6)$$

$$\left(1 - \frac{dy_j}{dx_j}\right) = -\frac{\Delta H}{RT^2} \frac{dT}{dx_j} \qquad (6a)$$

Since ΔH is the latent heat of vaporization of pure j and independent of the identities of other components, this relationship essentially defines the effect of trace amounts of other components in liquid on the vapor composition as well as the bubble point. For the same component j, data points of dy_j/dx_j vs. dT/dx_j for various mixtures with all non-j components at the infinite dilution should fall on a straight line with a slope corresponding to $-\Delta H/RT^2$ and an intercept of 1. Within the accuracy of graphical operations and known latent heat of component j, Equation (6*a*) may be used to test the consistency of equilibrium data at the point of infinite dilution. Nonideality of the vapor phase has no effect on (6*a*).

Composition Approaching an Azeotrope

Equation (5) may be rearranged to the form of Equation (7) of which each term on the left side is indeterminate due to a flat temperature profile at the azeotropic composition. Consequently, Equation (7*a*) is obtained with the indeterminancy eliminated by using L'Hopital rule:

$$\sum_i (x_i - y_i)(d\ln f_i^V/dT) = \Delta H/RT^2 \qquad (7)$$

$$\sum_i 1/[d(dT/d\ln f_i^V)/d(x_i - y_i)] = \Delta H/RT^2 \qquad (7a)$$

Since Equation (7*a*) involves two differential operations, calculation results would have a larger error than those of the nonazeotropic mixtures using Equation (5).

At the Critical Point

At the critical point the equivalent form of Equation (5) is Equation (7) in which all $x_i - y_i$ should vanish. The term $d \ln f_i^V/dT$ equals $(1/y_i)$ (dy_i/dT) and $(1/\phi_i)$ $(d\phi_i/dT)$ with dy_i/dT and $(1/\phi_i)$ $(d\phi_i/dT)$ being finite. Therefore, $\Delta H/RT^2$ must vanish or the latent heat of vaporization is zero at the critical point. This is certainly the expected property of any mixture at the critical point.

EXAMPLE 1

The ethanol-water system at 760 mm. mercury is chosen because of the following reasons:

1. The low pressure may permit the use of y_iP in place of fugacity f_i so that computation will be less time consuming.
2. The enthalpy data of the system was known (5) and can be compared with the numerical results obtained from the proposed equation.
3. The vapor composition was calculated from the bubble point data (*19*) and was found to agree fairly well with experimental results. The computation results here would thus demonstrate an extension of thermodynamic property from the minimum amount of experimental data.

Equation (8) is the transformed equation for a binary system with $\phi_i = 1.0$. Figure 3 indicates the general shape of $(x_i - y_i)/y_i$ for this binary. For any nonazeotropic system, these functions are unimodal. Equation (8) may be further simplified to Equation (9) for the present computation. Therefore

$$\frac{x_1 - y_1}{y_1}\frac{dy_1}{dT} + \frac{x_2 - y_2}{y_2}\frac{dy_2}{dT} = \frac{\Delta H - \Delta H^*}{RT^2} \qquad (8)$$

$$\Delta H - \Delta H^* = (RT^2)\left(\frac{x_1}{y_1} - \frac{x_2}{y_2}\right)\left(\frac{dy_1}{dT}\right) \qquad (9)$$

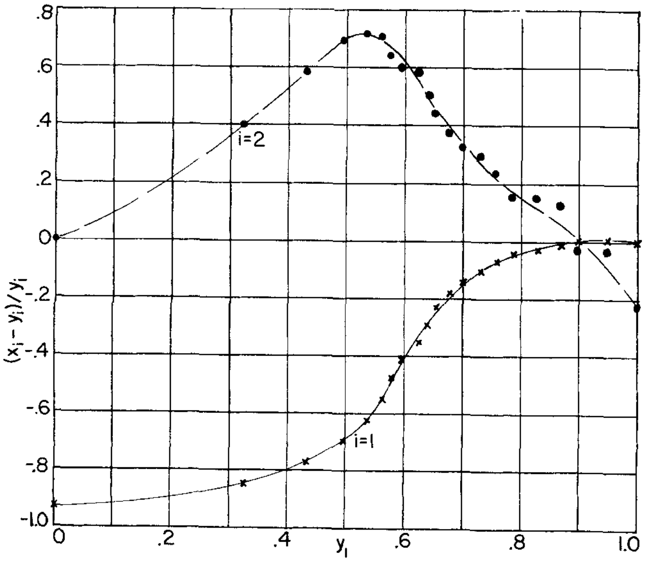

Fig. 3. Composition function [Equation (10)] of ethanol-water system.

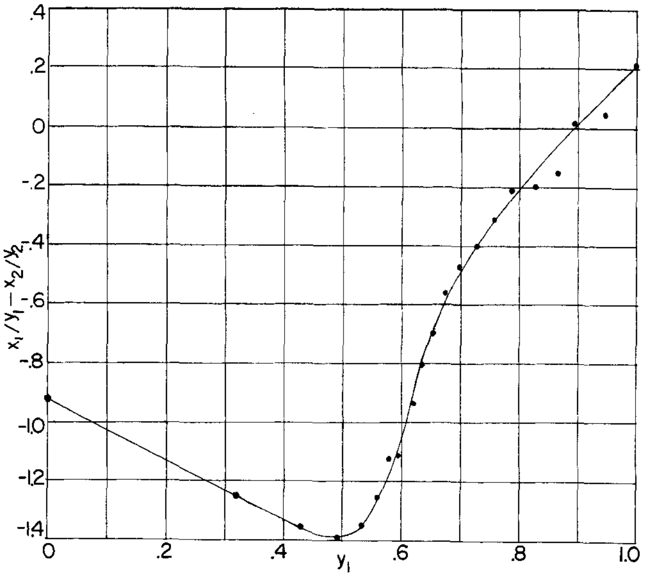

Fig. 4. Composition function [Equation (11)] of ethanol-water system.

Figures 4 and 5 show the calculated points and curves. These curves are not as well-behaved as those of the excess free energy surface. Consequently, application of the trapezoidal rule for integration may cause large error in the region having large curvatures. Figure 6 shows the terminal slopes from which the heat of vaporization of pure components are calculated.

Since the vapor phase is assumed to be ideal gas or $H^V = H^*(y)$, the term $(\Delta H - \Delta H^*)$ would be the integral heat of vaporization at x_1. Table 1 shows the computation results of Equation (9). The magnitudes of deviations of the calculated values are reasonably good if we consider all probable errors involved here starting from the bubble temperature curve as the only data source.

For a multicomponent system a smooth composition path passing the point of interest must be at first chosen to yield preferably some convenient, monotonic functions of fugacities vs. temperature. Then the $d \ln f_i/dT$ terms for estimating ΔH may be calculated analogously to that of a binary system. Another possibility would be to use trapezoidal rule in Equation (5) to solve the average ΔH between two close-by points.

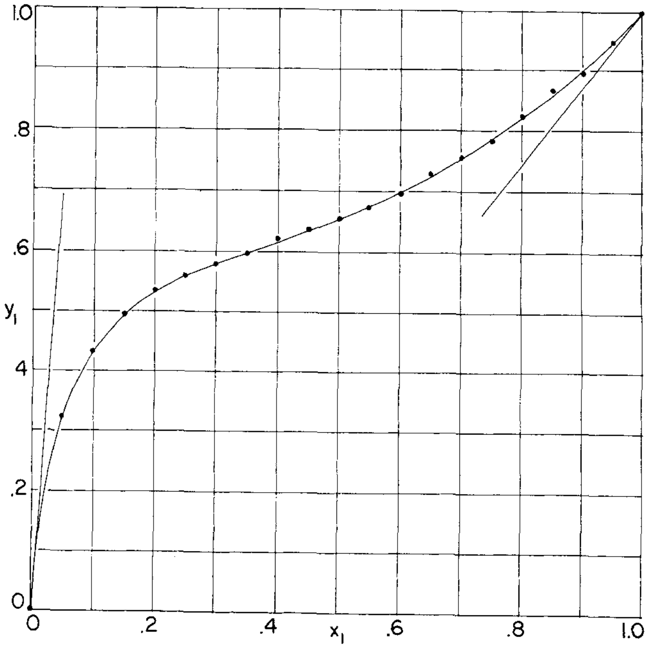

Fig. 5. *x — y diagram and terminal slopes of ethanol-water system.*

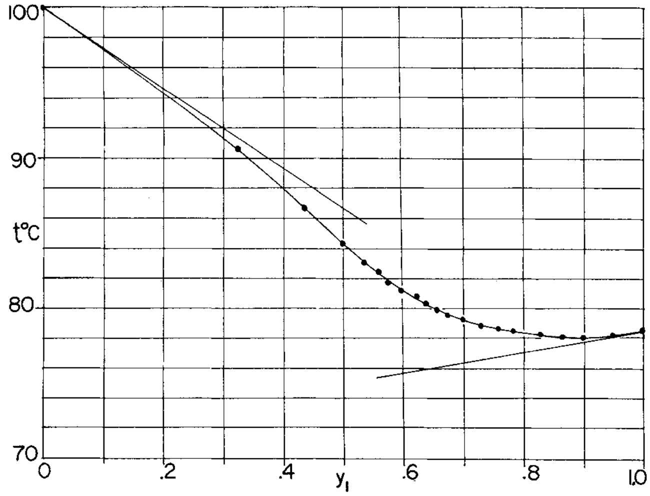

Fig. 6. *y — t diagram and terminal slopes of ethanol-water system.*

where

$$\beta_i = x_i \Bigg/ \sum_{k\neq 1} x_k \tag{10}$$

The ternary system of toluene(1)-heptane(2)-cyclohexane(3) reported by Myers and Hipkins (*7*, *13*, *14*) is used here to illustrate the utility of Equations (6*a*) and (10) in the vicinity of pure toluene. The experimental values of dy_1/dx_1 for binaries were measured graphically from the *x*-*y* plots and those of ternaries were calculated from the differences. The corresponding calculated values refer to those estimated from Equation (6*a*) using the experimental dT/dx_1 and ΔH = 7,997 cal./g. mole of toluene (*16*).

Also, using the maximum experimental error of 0.002 for mole fractions of trace elements and that of 0.1°C. for the temperature measurement, the error ranges can be estimated. Figure 7 shows that the temperature measurements appear to be less reliable than the composition measurements in the ternary region while the binary data are consistent within errors of graphical operations.

TABLE 1. A COMPARISON OF ΔH CALCULATED FROM EQUATION (5) AND DATA

System: ethanol (1)-water (2) at 760 mm. mercury

x_1	y_1(19)	T °K.	$x_1/y_1 - x_2/y_2$	dy_1/dT	ΔH, cal./g. mole Equation (9)	data (5)	% error
0	0	373.16	−0.930	−0.0375	9,649	9,712	−0.7
0.1	0.432	359.96	−1.3530	−0.0274	9,545	9,930	−3.9
0.2	0.534	356.36	−1.3422	−0.0280	9,483	10,844	−12.6
0.3	0.575	354.96	−1.1254	−0.0345	9,720	9,900	−1.9
0.4	0.621	353.96	−0.9390	−0.0440	10,285	9,770	+5.2
0.5	0.654	353.16	−0.6806	−0.0530	8,950	9,660	−7.4
0.6	0.698	352.51	−0.4909	−0.0758	9,162	9,580	−4.4
0.7	0.757	351.92	−0.3099	−0.1240	9,456	9,550	−1.1
0.8	0.827	351.53	−0.1887	−0.2128	9,860	9,560	+3.1
1.0	1.000	351.48	0.220	+0.172	9,289	9,398	−1.2

EXAMPLE 2

For a multicomponent system in the vicinity of a pure component 1, each of the trace component molecules would be caged by molecules of component 1 in the same way as a single trace component of a binary system. Therefore, interaction between different trace components cannot exist and the vaporization of component 1 in a mixture would be Equation (10) which shows a linear combination of binary vaporization ratios $(dy_1/dx_1)_i$ of the 1*i* binary. It can be proved by letting $x_i = dx_i$.

$$dy_1/dx_1 = \sum_{i\neq 1} \beta_i \, (dy_1/dx_1)_i$$

DISCUSSION

Equation (5) is rigorous, straight forward and applicable to multicomponent systems. Example 1 indicates that this equation may be used to estimate the enthalpy differences between phases directly from *x*-*y*-*T* data. Further investigation should be made to use fugacities, especially for the high pressure region, in calculating the enthalpy differences. The accuracy and precision of the estimated values are highly dependent of the availability of P-V-T-*y* data or equations of state and the inherent error of differentiation operation. However, all available methods have similar implications. The advantages of this equation are simplicity, applicability in multicomponent systems, and utilization of the minimum amount of experi-

TABLE 2. CALCULATION RESULTS OF TESTING CONSISTENCY OF TOLUENE(1)-HEPTANE(2)-CYCLOHEXANE(3) SYSTEM IN THE VICINITY OF PURE TOLUENE

t °C.	x_2	x_3	β_2	dy_1/dx_1 expt.*	error range	calculated from temp. data†	reference
110.6	—	—	1.000	1.80	—	1.87	*7*
107.6	0.071	0.014	0.835	1.849	1.720 to 1.988	1.941 to 2.097	*14*
107.7	0.039	0.018	0.684	2.088	1.885 to 2.321	2.340 to 2.650	*14*
104.7	0.028	0.079	0.354	2.224	2.108 to 2.350	2.474 to 2.640	*14*
110.6	—	—	0.000	2.50	—	2.56	*13*

* $dy_1/dx_1 = (1 - y_1)/(1 - x_1)$.
† $dy_1/dx_1 = -(\Delta H/RT^2)(110.6 - t)/(1 - x_1)$.

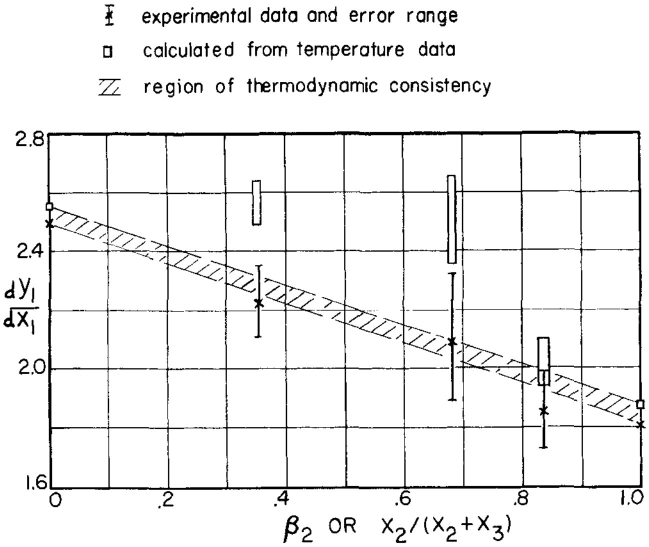

Fig. 7. Vaporization ratio of toluene (1) in trace mixtures of heptane (2) and cyclohexane (3) at 760 mm. Hg.

mental data. Also, the latent heat thus obtained would be thermodynamically consistent with the composition data.

Equation (6*a*) as a limiting case of Equation (5) may be considered as the generalized form of the Gautreaux and Coates equations (*6*) which are valid for binary systems only. Example 2 exhibited the use of this equation. The vaporization ratio from Equation (6*a*) would be useful in purification operation of component 1 with impurities.

The total derivatives in Equation (5) also imply that this equation is applicable in any direction of a composition space. The directional change of phase composition depends on the derivatives of gas phase fugacities in the same direction. Therefore, this suggests that an average ΔH value may be obtained by using Equation (5) along paths linking several surrounding points toward a center one. If ΔH value does not vary greatly, Equation (5) may also be used to test the consistency of experimental data among points by using Equation (11) for two points and Equation (12) for three points in two pairs. Thus

$$\left[T^2 \sum_i (x_i - y_i)\, d\ln f_i/dT\right]_{\text{point a}} = \left[T^2 \sum_i (x_i - y_i)\, d\ln f_i/dT\right]_{\text{point b}} \tag{11}$$

$$[T_aT_b/(T_b - T_a)] \int_a^b \sum_i (x_i - y_i)\, d\ln f_i = [T_aT_c/(T_c - T_b)] \int_a^c \sum_i (x_i - y_i)\, d\ln f_i \tag{12}$$

The main difference between these equations and the commonly used Gibbs-Duhem equation is the elimination of the use of the liquid phase activity coefficients in the former. For low pressure systems, $d\ln f_i = d\ln y_i$ would further simplify the computation. The validity of these equations depends on whether the variation of ΔH is negligible as previously assumed.

CONCLUSION

An equation shown by van Ness (*12*) is extended and analyzed for studies of vapor-liquid equilibrium. Many potential uses are cited and some illustrated. These include estimation of latent heat of vaporization from x-y-T data, consistency test of phase composition and enthalpy data, and predicting the equilibrium condition of a multicomponent system in the vicinity of a pure component.

NOTATION

f = fugacity
H = molar enthalpy with the datumn state at 0°K.
P = total pressure
R = gas constant
T = absolute temperature in °K. = t°C. + 273.16
V = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
β = trace component fraction among all trace components
Δ = difference between the saturated vapor and the liquid of the same tie line
γ = component activity coefficient in liquid phase
ϕ = component fugacity coefficient in vapor

Superscripts

L = liquid phase
V = vapor phase
o = standard state
$*$ = assumed ideal-gas state at 1.0 atm. pressure

Subscripts

a, b, c = identity of mixture composition
1, 2, i, j = component identity
M = mixing, difference between mixture property and the sum of properties of species at standard states weighted according to the respective mole fractions of the species

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