Activity Coefficients at Infinite Dilution

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Equations are derived for obtaining activity coefficients at infinite dilution in binary systems by use of one of the following: (1) an isobaric temperature—liquid composition diagram, (2) an isobaric temperature—vapor composition diagram, (3) an isothermal pressure—liquid composition diagram, or (4) an isothermal pressure—vapor composition diagram. The derived equations are thermodynamically exact, and application involves no doubtful extrapolation of experimental data, as has heretofore been the case.

Each equation involves the slope of one of the diagrams at the point corresponding to the pure component. Attention is called to the fact that data on the compositions of both the vapor and liquid phases in equilibrium are not required. Use of the equations is illustrated.

Vapor-liquid equilibrium data are frequently correlated in terms of activity coefficients. An activity coefficient, γ, is a thermodynamic quantity which is related to the fugacity, f, of a component in solution by an expression such as Equation (1):

$$\gamma_{1L} = \frac{f_{1L}}{x_1 f^{o}_{1L}} \qquad (1)$$

Subscript 1 refers to component one; subscript L refers to the liquid phase. [An equation analogous to Equation (1) could be written for component one in the vapor phase.] The subscript 0 refers to the chosen standard state. It is convenient to choose pure liquid and pure vapor at the temperature and pressure of the system for liquid- and vapor-phase standard states, respectively. These standard states are used throughout this paper. Usually at the temperature and pressure of the system the pure component will be either liquid or vapor, and one of the standard states will be hypothetical.

As the mole fraction of component one approaches zero in solution, its activity coefficient approaches a definite limit. This limiting value is frequently termed the "activity coefficient of component one at infinite dilution." The condition of infinite dilution will be designated by the subscript $x_1 = 0$. Thus

$$(\gamma_{1L})_{x_1=0} = \lim_{x_1 \to 0} \gamma_{1L} \qquad (2)$$

This coefficient is of considerable practical and theoretical interest. In extractive and azeotropic distillations important components frequently appear in very low concentrations in the liquid phase. The activity coefficient at infinite dilution is of aid in the determination of vapor-liquid equilibrium in these regions. Similarly the activity coefficient at infinite dilution is important because its logarithm generally appears as a constant in empirical equations which relate log γ and x (*1*). The coefficient is of interest to the scientist who is attempting to relate the structures of pure components and the nonidealities of solutions. This relation is probably most easily made at infinite dilution where there is absolutely no interaction among solute molecules in solution (*10*). Thus the partial molal excess free energy at infinite dilution is obtained (*3*) directly from Equation (3):

$$(\bar{G}^E = RT \ln \gamma)_{x=0} \qquad (3)$$

The partial molal excess enthalpy at infinite dilution is obtained by determining the rate of change of the coefficient with temperature:

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TABLE 1.—EXACT EQUATIONS FOR $(\gamma_{1L}/\gamma_{1V})_{x_1=0}$

Type of diagram	Applicable thermodynamically exact equation* $(\gamma_{1L}/\gamma_{1V})_{x_1=0}$ equals	Applicable low-pressure equation* $(\gamma_{1L})_{x_1=0}$ equals
I. Isobaric temperature–liquid composition diagram†	$\frac{f^o_{1V}}{f^o_{1L}}\left[1-\left(\frac{\partial T}{\partial x_1}\right)_\pi\left(\frac{d\ln P_2}{dT}\right)\left(\frac{V_{2V}\pi}{RT}-\frac{V_{2L}\pi}{RT}\right)\right]$	$\frac{\pi}{P_1}\left[1-\left(\frac{\partial T}{\partial x_1}\right)_\pi\left(\frac{d\ln P_2}{dT}\right)\right]$
II. Isobaric temperature–vapor composition diagram†	$\frac{f^o_{1V}}{f^o_{1L}}\left[\frac{1}{1+\left(\frac{\partial T}{\partial y_1}\right)_\pi\left(\frac{d\ln P_2}{dT}\right)\left(\frac{V_{2V}\pi}{RT}-\frac{V_{2L}\pi}{RT}\right)}\right]$	$\frac{\pi}{P_1}\left[\frac{1}{1+\left(\frac{\partial T}{\partial y_1}\right)_\pi\left(\frac{d\ln P_2}{dT}\right)}\right]$
III. Isothermal pressure–liquid composition diagram	$\frac{f^o_{1V}}{f^o_{1L}}\left[1+\left(\frac{\partial \pi}{\partial x_1}\right)_T\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right)\right]$	$\frac{\pi}{P_1}\left[1+\frac{1}{\pi}\left(\frac{\partial \pi}{\partial x_1}\right)_T\right]$
IV. Isothermal pressure–vapor composition diagram	$\frac{f^o_{1V}}{f^o_{1L}}\left[\frac{1}{1-\left(\frac{\partial \pi}{\partial y_1}\right)_T\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right)}\right]$	$\frac{\pi}{P_1}\left[\frac{1}{1-\frac{1}{\pi}\left(\frac{\partial \pi}{\partial y_1}\right)_T}\right]$

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*All terms evaluated at conditions corresponding to $x_1 = 0$.

†$\frac{d\ln P_2}{dT}\left(\frac{V_{2V}\pi}{RT}-\frac{V_{2L}\pi}{RT}\right)\frac{\lambda_2}{RT^2}$ (Clapeyron equation)

$$\left[\left(\frac{\partial \ln \gamma}{\partial T}\right)_\pi = \frac{-\bar{H}^E}{RT^2}\right]_{x=0} \quad (4)$$

And the partial molal excess entropy can then be obtained from

$$(\bar{G}^E = \bar{H}^E - T\bar{S}^E)_{x=0} \quad (5)$$

Activity coefficients at infinite dilution have been calculated in a variety of ways, perhaps most frequently from van Laar or similar constants obtained after vapor-liquid equilibrium data were correlated. For example, the van Laar constant A is related to the activity coefficient of component one (*3*) by the equation

$$A = (\log \gamma_{1L})_{x_1=0} \quad (6)$$

If vapor-liquid equilibrium data are available in the region $x_1 = 0$, graphical extrapolation by eye of γ_{1L} to $x_1 = 0$ is often used to obtain $(\gamma_{1L})x_1 = 0$. Carlson and Colburn (*1*) suggest using an isothermal pressure-composition diagram or an isobaric temperature-composition diagram and calculating an "apparent" activity coefficient which may be extrapolated to $x_1 = 0$ to obtain $(\gamma_{1L})x_1 = 0$.

The object of this paper is to derive *thermodynamically exact* relations for activity coefficient at infinite dilution in binary systems. No assumptions will be made concerning the idealities of the vapors or the vapor-phase solutions. Nor will the assumptions be made of a negligible heat of mixing and of a negligible effect of temperature on activity coefficients. Relations will be derived for utilization of vapor-liquid equilibrium data, isobaric temperature-composition diagrams, and isothermal pressure-composition diagrams. Usually it is simpler experimentally to obtain the two diagrams.

DERIVATION OF EQUATIONS

At equilibrium, $f_{1L} = f_{1V}$, Equation (7) results:

$$\frac{\gamma_{1L}}{\gamma_{1V}} = \frac{y_1 f^o_{1V}}{x_1 f^o_{1L}} \quad (7)$$

As x_1 approaches zero, the right-hand member (RHM) approaches the form 0/0. Applying L'Hospital's rule yields

$$\left(\frac{\gamma_{1L}}{\gamma_{1V}}\right)_{x_1=0} = \left[\left(\frac{\partial y_1}{\partial x_1}\right)\left(\frac{f^o_{1V}}{f^o_{1L}}\right)\right]_{x_1=0}$$

$$= \left[K_1\left(\frac{f^o_{1V}}{f^o_{1L}}\right)\right]_{x_1=0} \quad (8)$$

where K is the familiar equilibrium vaporization ratio.

Equation (8) is an exact thermodynamic relation for $(\gamma_{1L}/\gamma_{1V}) x_1 = 0$. It is independent of the number of components under consideration and applies to both constant temperature and constant pressure data. However, Equation (8) involves determinations of y and x in equilibrium at low values of y and x. These determinations are experimentally difficult.

Further derivations will be made to obtain $(\gamma_{1L}/\gamma_{1V})x_1 = 0$ in terms of information available from the more easily obtained isobaric temperature-composition diagrams and isothermal pressure-composition diagrams. A binary system will be considered.

When an equation for component two analogous to Equation (7) is utilized,

$$y_1 = 1 - y_2 = \frac{\gamma_{2V} f^o_{2V} - \gamma_{2L} x_2 f^o_{2L}}{\gamma_{2V} f^o_{2V}} \quad (9)$$

Differentiating with respect to x_1 and noting that at $x_1 = 0$, $\gamma_{2V} = \gamma_{2L} = 1.0$, $f_{2V}{}^\circ = f_{2L}{}^\circ = f_2{}^\circ$, $\partial\gamma_{2V}/\partial x_1$

Table 2.—Exact Relations Between $\partial T/\partial x_1$ and $\partial T/\partial y_1$ and $\partial \pi/\partial x_1$ and $\partial \pi/\partial y_1$

Type of diagram	Relation*
I. Isobaric temperature-composition diagram	$\frac{1}{\left(\frac{\partial T}{\partial x_1}\right)_\pi} - \frac{1}{\left(\frac{\partial T}{\partial y_1}\right)_\pi} - \frac{d \ln P_2}{dT}\left(\frac{V_{2V}\pi}{RT} - \frac{V_{2L}\pi}{RT}\right) = 0$
II. Isothermal pressure-composition diagram	$\frac{1}{\left(\frac{\partial \pi}{\partial x_1}\right)_T} - \frac{1}{\left(\frac{\partial \pi}{\partial y_1}\right)_T} + \left(\frac{V_{2V}}{RT} - \frac{V_{2L}}{RT}\right) = 0$

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*All terms evaluated at conditions corresponding to $x_1 = 0$.

$= \partial\gamma_{2L}/\partial x_1 = 0$ (*see* Appendix 4) gives Equation (10):

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} = \left[\frac{f_2^o + \frac{\partial (f^o_{2V} - f^o_{2L})}{\partial x_1}}{f_2^o}\right]_{x_1=0} \tag{10}$$

This equation is applicable to both constant-pressure and constant-temperature data.

At constant pressure one may write

$$\left[\frac{\partial (f^o_{2V} - f^o_{2L})}{\partial x_1}\right]_\pi = \left[\frac{\partial (f^o_{2V} - f^o_{2L})}{\partial T}\right]_\pi \left(\frac{\partial T}{\partial x_1}\right)_\pi \tag{11}$$

where $\partial T/\partial x_1$ will be recognized as the slope of an isobaric temperature-liquid composition diagram. As a result of the standard states chosen, the following thermodynamically exact expressions apply:

$$f^o_{2V} = \nu_{\pi,\,T}\,\pi \tag{12}$$

$$f^o_{2L} = \nu_{P_2,\,T}\, P_2 e^{V'_{2L}(\pi - P_2)/RT} \tag{13}$$

When (12) and (13) are utilized in Equation (11) at $x_1 = 0$, Equation (14) results:

$$\left\{\left[\frac{\partial (f^o_{2V} - f^o_{2L})}{\partial x_1}\right]_\pi = f_2^o \left(\frac{\partial T}{\partial x_1}\right)_\pi \left(-\frac{d \ln P_2}{dT}\right)\left(\frac{\pi V_{2V}}{RT} - \frac{\pi V_{2L}}{RT}\right)\right\}_{x_1=0} \tag{14}$$

Combining (14), (10) and (8) yields the desired result:

$$\left\{\frac{\gamma_{1L}}{\gamma_{1V}} = \frac{f^o_{1V}}{f^o_{1L}}\left[1 - \left(\frac{\partial T}{\partial x_1}\right)_\pi \left(\frac{d \ln P_2}{dT}\right)\left(\frac{\pi V_{2V}}{RT} - \frac{\pi V_{2L}}{RT}\right)\right]\right\}_{x_1=0} \tag{15}$$

Equation (15) is a thermodynamically exact relation for obtaining $(\gamma_{1L}/\gamma_{1V})x_1 = 0$ from the slope of an isobaric temperature-liquid composition diagram at $x_1 = 0$.

By mathematics paralleling that above, equations can be derived which utilize slopes at infinite dilution of an isobaric temperature-vapor composition diagram, an isothermal pressure-liquid composition diagram, and an isothermal pressure-vapor composition diagram. Table 1 summarizes these equations.

As previously noted, there are no assumptions involved in the equations of Table 1. They apply even if the pure vapors are nonideal and if the vapors form a nonideal solution. Furthermore, the effect of temperature on liquid phase activity coefficients has not been neglected.

Redlich and Kister(*8*) have derived relations among $\partial T/\partial x$ and $\partial T/\partial y$, the relative volatility and vapor pressures. Their derivations were made for conditions of low pressure, negligible effect of temperature on activity coefficients and

Table 3.—Exact Equations for Calculating K_1 at $x_1 = 0$

Type of diagram	Equation*
I. Isobaric temperature–liquid composition diagram	$1 - \left(\frac{\partial T}{\partial x_1}\right)_\pi \left(\frac{d \ln P_2}{dT}\right)\left(\frac{V_{2V}\pi}{RT} - \frac{V_{2L}\pi}{RT}\right)$
II. Isobaric temperature–vapor composition diagram	$\frac{1}{1 + \left(\frac{\partial T}{\partial y_1}\right)_\pi \left(\frac{d \ln P_2}{dT}\right)\left(\frac{V_{2V}\pi}{RT} - \frac{V_{2L}\pi}{RT}\right)}$
III. Isothermal pressure–liquid composition diagram	$1 + \left(\frac{\partial \pi}{\partial x_1}\right)_T \left(\frac{V_{2V}}{RT} - \frac{V_{2L}}{RT}\right)$
IV. Isothermal pressure–vapor composition diagram	$\frac{1}{1 - \left(\frac{\partial \pi}{\partial y_1}\right)_T \left(\frac{V_{2V}}{RT} - \frac{V_{2L}}{RT}\right)}$

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*All terms evaluated at conditions corresponding to $x_1 = 0$.

negligible effect of pressure on liquid-phase fugacities. Nord(*7*) derived an equation in terms of $\partial T/\partial y$ which can be reduced to the equation in terms of $\partial T/\partial y$ in Table 1. Nord's equation is thermodynamically exact except for the assumption that the vapor phase is an ideal solution. Ibl and Dodge (*4*) have derived thermodynamically exact equations in terms of $\partial \pi/\partial y$ and $\partial T/\partial y$ which can be used to derive the equations in Table 1 involving $\partial \pi/dy$ and $\partial T/dy$.

Combination of the equations in Table 1 yields relations between $\partial T/\partial x_1$ and $\partial T/\partial y_1$ and $\partial \pi/\partial x_1$ and $\partial \pi/\partial y_1$ which must be fulfilled for thermodynamic consistency. These relations are summarized in Table 2.

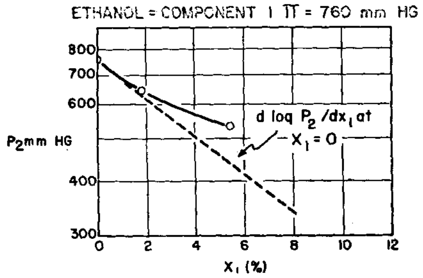

Fig. 1. Plot of P_2 vs. x_1 at 760 mm. Hg for ethanol (component 1)—water. Dotted line is $(\partial \log P/\partial x_1)\pi$ at $x_1 = 0$.

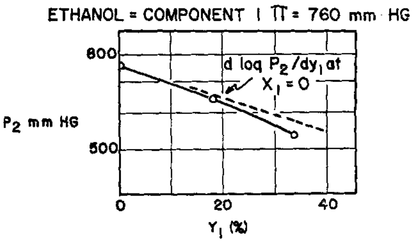

Fig. 2. Plot of log P_2 vs. y_1 at 760 mm. Hg. Dotted line is $(\partial \log P_2/\partial y_1)\pi$ at $x_1 = 0$.

Combining equations such as (15) and (8) makes it possible to determine $(K_1)_{x_1=0}$. These relations are summarized in Table 3. Thus the slope of the *x-y* diagram is also rigorously determined at $x_1 = 0$. It is important to note that it frequently happens that at the temperature and pressure corresponding to pure component two, component one will have a hypothetical standard state. This factor has no bearing on the relations in Table 2 or 3. Indeed, the relations are valid even if component one is above its critical point at the condition corresponding to $x_1 = 0$.

The relations in Tables 2 and 3 serve as thermodynamic consistency checks when vapor-liquid equilibrium data are available. These relations are exact. Indeed they are the only *exact* relations which are applicable when just vapor-liquid equilibrium data and pure component data are available. For example, the *exact* application of the Gibbs-Duhem equation at other values of *x* requires knowledge of the vapor-phase-solution nonideality and either the heat of mixing (isobaric data) or volume change upon mixing (isothermal data) (*2*, *4*, and *7*).

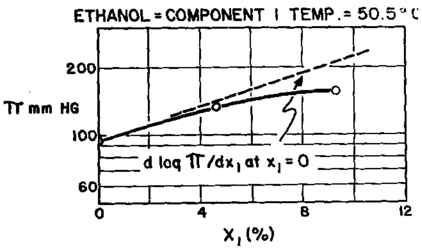

Fig. 3. Plot of log π vs. x_1 at 50.5°C. for ethanol (component 1)—water. Dotted line is $(\partial \log \pi/\partial x_1)_T$ at $x_1 = 0$.

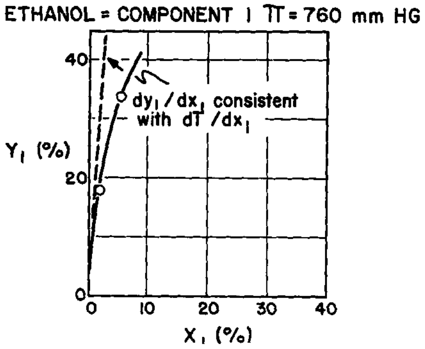

Fig. 4. *x-y* diagram for ethanol (component 1)—water at 760 mm. Hg. Dotted line is $(\partial y_1/\partial x_1)\pi$ thermodynamically consistent with $(\partial T/\partial x_1)\pi$.

Latent heats of vaporization may be rigorously introduced by the relation in a footnote to Table 1.

At low pressures $f^\circ_{1V} = \pi, f^\circ_{1L} = P_1$, $V_{2L}\pi/RT << 1.0$, $V_{2V}\pi/RT$ approaches unity, and γ_{1V} approaches unity. The exact equations in Table 1 then reduce to the "low-pressure" equations tabulated in the last column of Table 1.

The equations for isobaric and isothermal data may be put in similar forms by simple rearrangement. As an illustration for liquid composition diagrams at $x_1 = 0$:

Isobaric:

$$\left\{\frac{\gamma_{1L}}{\gamma_{1V}} = \frac{f^o_{1V}}{f^o_{1L}}\left[1 - \left(\frac{\partial \ln P_2}{\partial x_1}\right)_\pi \left(\frac{V_{2V}\pi}{RT} - \frac{V_{2L}\pi}{RT}\right)\right]\right\}_{x_1=0} \quad (16$$

Isothermal:

$$\left\{\frac{\gamma_{1L}}{\gamma_{1V}} = \frac{f^o_{1V}}{f^o_{1L}}\left[1 + \left(\frac{\partial \ln \pi}{\partial x_1}\right)_T \left(\frac{V_{2V}\pi}{RT} - \frac{V_{2L}\pi}{RT}\right)\right]\right\}_{x_1=0} \quad (17$$

Illustrative Example

Application of the derived equations to experimental data is not difficult. The isobaric and isothermal data of Jones, Schoenborn and Colburn(*5*) for ethanol-water is used here. Ethanol has been chosen as component one.

TABLE 4.—ISOBARIC AND ISOTHERMAL DATA FOR ETHANOL-WATER*

Isobaric at 760 mm.Hg

Temp., °C.	x_1	y_1
100	0	0
95.5	0.018	0.179
90.6	0.054	0.338

Isothermal at 50.5°C.

Press., mm.Hg	x_1	y_1
94.8	0	0
133	0.046	0.290
157	0.093	0.424

*Ethanol is component *1*.

Isobaric Data. T-x_1 data are in Table 4 for 760 mm.Hg total pressure. One has the option of plotting T vs. x_1 and obtaining $(\partial T/\partial x_1)\pi$ at $x_1 = 0$, or of obtaining P_2 for each value of x_1 and plotting ln P_2 vs. x_1 and obtaining $(\partial \ln P_2/\partial x_1)\pi$. The latter route, which usually results in more accurate slope taking, is used in Figure 1 with the vapor pressure of water from Keenan(*6*).

From Figure 1 $(\partial \ln P_2/\partial x_1)\pi = -14.34$; and, with the appropriate "low-pressure" equation and the vapor pressure of ethanol from Stull(*9*),

$$\left\{\gamma_{1L} = \frac{\pi}{P_1}\left[1 - \left(\frac{\partial \ln P_2}{\partial x_1}\right)_\pi\right]\right\}_{x_1=0} \quad (18)$$

$$(\gamma_{1L})_{x_1=0} = \frac{760}{1,685}(15.34) = 6.92 \quad (18a)$$

[This value is a reasonable extrapolation of the plot of log γ_{1L} vs.

x_1 in the original reference(*5*).]

In Figure 2 $(\partial \ln P_2/\partial y_1)_\pi$ has been determined as —0.846. With the appropriate low-pressure equation.

$$\left\{\gamma_{1L} = \frac{\pi}{P_1}\left[\frac{1}{1+\left(\frac{\partial \ln P_2}{\partial y_1}\right)_\pi}\right]\right\}_{x_1=0} \tag{19}$$

$$(\gamma_{1L})_{x_1=0} = \frac{760}{1{,}685\ (0.154)} = 2.93 \tag{19a}$$

This brings out an important point. The value 2.93 is not close to 6.92; however, determination by means of $(\partial \ln P_2/\partial y_1)_\pi$ is subject to considerable error because the *difference* between unity and $(-\partial \ln P_2/\partial y_1)_\pi$ is involved. Thus, using $(\partial \ln P_2/\partial y_1)_\pi$ is not a desirable route. This conclusion is valid for all systems wherein $(\partial \ln P_2/\partial y_1)_\pi$ is *negative* (e.g., minimum boiling azeotropes). For systems where $(\partial \ln P_2/\partial y_1)_\pi$ is *positive,* use of $(\partial \ln P_2/\partial y_1)_\pi$ is preferred. Similar considerations apply when constant-temperature data are used.

Isothermal Data. In Figure 3 $(\partial \ln \pi/\partial x_1)_T$ is determined for the 50.5°C. data. With the appropriate low-presure equation, $\gamma_{1L} = 4.01$. [This value is a reasonable extrapolation of the plot of log γ_{1L} vs. x_1 in the original reference(*5*).]

Consistency Check. To illustrate a thermodynamic consistency check, the value of $(\partial y_1/\partial x_1)_\pi$ consistent with $(\partial T/\partial x_1)_\pi$ is shown in Figure 4 for the 760 mm.Hg data. There is clearly no inconsistency. Other checks which can be made are $(\partial T/\partial y_1)_\pi$ consistent with $(\partial T/\partial x_1)_\pi$ (and vice versa), by means of Table 3; $(\partial y_1/\partial x_1)_\pi$ consistent with $(\partial T/\partial y_1)_\pi$; and a similar set of checks for the isothermal data.

Discussion

Several additional points warrant comment.

The meager data required to establish these slopes are emphasized. Only two experimental points are required for the mixtures, and the composition of only a single phase need be considered.

The equations provide certain limits for any particular system. For example, since $(\gamma_{1L}/\gamma_{1V})$ must be positive, $(\partial T/\partial x_1)_{\pi_{x_1=0}}$ has a certain maximum value above which it cannot go.

To date little use has been made of isothermal pressure–liquid composition and isobaric temperature–liquid composition diagrams. The derived equations strongly suggest more use of these at least to obtain activity coefficients at infinite dilution.

ACKNOWLEDGMENT

The authors wish to acknowledge a critical review of this paper by L. C. Matsch and J. Wang of Linde Air Products.

NOTATION

A = dimensionless constant in the van Laar equation
e = base of natural logarithms
f = fugacity, atm.
G^E = excess free energy, B.t.u./lb.-mole
H^E = excess enthalpy, B.t.u./lb.-mole
K = equilibrium vaporization ratio $= y/x$
P = vapor pressure of a pure component, atm.
R = gas-law constant=1.987 B.t.u. / (lb.-mole) (°R.)
S^E = excess entropy, B.t.u./(lb.-mole) (°R.)
T = absolute temperature, °R.
V = molal volume of pure component, cu.ft./lb.-mole
V' = an average molal volume of the pure component over the pressure range π to P, cu.ft./lb.-mole
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
λ = latent heat of vaporization, B.t.u./lb.-mole
ν = fugacity coefficient $= f/\pi$
π = total pressure of the system, atm.

Subscripts

1, 2 refers to components one and two
L refers to liquid phase
V refers to vapor phase
$x_1 = 0$ refers to conditions at $x_1=0$
π, T and
P_2, T refer to the temperatures and pressures at which fugacity coefficients are evaluated

Superscripts

° refers to the standard state
— denotes a partial molal quantity (e.g., $\overline{G^E}$)

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APPENDIX

Proof That $(\partial \gamma_{2L}/\partial x_1)_\pi$ Equals Zero at $x_1 = 0$

γ_{2L} is a function of T, π, and x_1. Therefore

$$d \ln \gamma_{2L} = \left(\frac{\partial \ln \gamma_{2L}}{\partial T}\right)_{\pi,\ x_1} dT + \left(\frac{\partial \ln \gamma_{2L}}{\partial \pi}\right)_{T,\ x_1} d\pi + \left(\frac{\partial \ln \gamma_{2L}}{\partial x_1}\right)_{T,\ \pi} dx_1 \tag{1}$$

For constant pressure

$$\left(\frac{\partial \ln \gamma_{2L}}{\partial x_1}\right)_\pi = \left(\frac{\partial \ln \gamma_{2L}}{\partial T}\right)_{\pi,\ x_1} \left(\frac{\partial T}{\partial x_1}\right)_\pi + \left(\frac{\partial \ln \gamma_{2L}}{\partial x_1}\right)_{T,\ \pi} \tag{2}$$

But at $x_1 = 0$

$$\left(\frac{\partial \ln \gamma_{2L}}{\partial T}\right)_{\pi,\ x_1} = -\left(\frac{\overline{H}_2 - H_2^o}{RT^2}\right) = 0 \tag{3}$$

$$\left(\frac{\partial \ln \gamma_{2L}}{\partial x_1}\right)_{T,\ \pi} = -\frac{x_1}{x_2}$$

$$\left(\frac{\partial \ln \gamma_{1L}}{\partial x_1}\right)_{T,\ \pi} = 0 \tag{4}$$

Thus,

$$\left(\frac{\partial \ln \gamma_{2L}}{\partial x_1}\right)_\pi = \frac{1}{\gamma_{2L}}\left(\frac{\partial \gamma_{2L}}{\partial x_1}\right)_\pi = \left(\frac{\partial \gamma_{2L}}{\partial x_1}\right)_\pi = 0 \qquad (5$$

A similar argument holds for $(\partial \gamma_{2V}/\partial x_1)_\pi$ at $x_1 = 0$. Also a similar argument holds if temperature rather than pressure is held constant.

(Presented at A.I.Ch.E. Houston meeting.)