

B. Liquid-Phase Activity Coefficients: Effect of Composition

For isothermal phase equilibria, the liquid-phase activity coefficient depends on the liquid-phase composition and also on the total pressure. For effective thermodynamic analysis and correlation of high-pressure vapor-liquid equilibrium data, it is important to separate the effect of pressure from that of composition. For a binary system, it is useful, therefore, to define two adjusted activity coefficients independent of pressure (25) by:

$$\gamma_1^{(P^r)} = \frac{f_1}{x_1 f_{\text{pure } 1}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_1^L}{RT} dP \quad (18)$$

and

$$\gamma_2^{*(P^r)} = \frac{f_2}{x_2 H_{2(1)}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_2^L}{RT} dP \quad (19)$$

where subscript 1 refers to the condensable and subscript 2 to the noncondensable component.

The fugacities, f_1 and f_2 , are those at the total pressure P of the system. The reference pressure P^r is arbitrary and is most conveniently set equal to zero. As shown elsewhere (25), the constant-pressure activity coefficients defined by Equations 18 and 19 satisfy the isothermal, isobaric Gibbs-Duhem equation:

$$x_1 d \ln \gamma_1^{(P^r)} + x_2 d \ln \gamma_2^{*(P^r)} = 0 \quad (20)$$

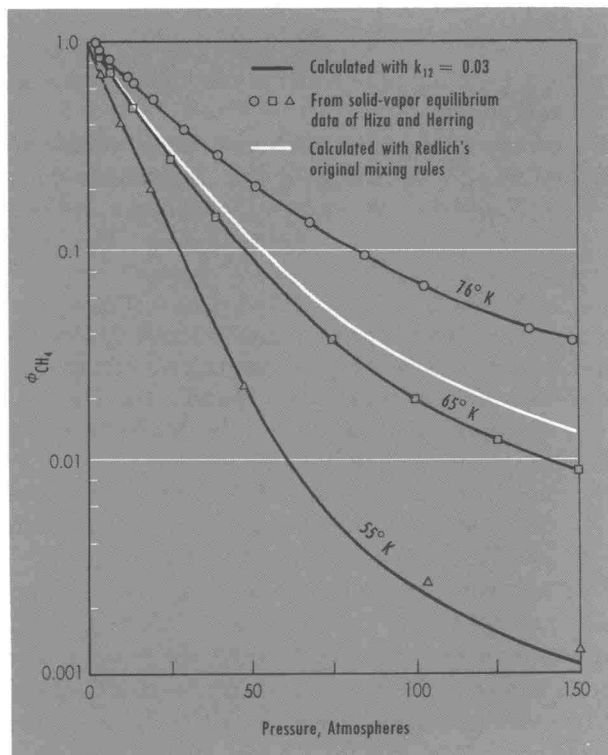


Figure 2. Fugacity coefficients of methane in hydrogen at saturation ($k_{12} = 0.03$ obtained from second virial coefficient data)

As a result, the composition dependence of these activity coefficients can be represented by an integrated form of Equation 20 (for example, the van Laar equation or the Margules equation) as commonly used in low-pressure vapor-liquid equilibria. Through the exponential factors in Equations 18 and 19 (the Poynting correction), the effect of pressure is separated from the effect of composition, and as a result, interpretation and correlation of high-pressure phase-equilibrium data are very much facilitated (25). A technique for calculating partial molar volumes \bar{v}_1^L and \bar{v}_2^L , required in Equations 18 and 19, is presented in Section C.

The asterisk (*) in Equation 19 is a reminder that the unsymmetric convention has been used for normalization of activity coefficients. For subcritical component 1 (the temperature T of the solution is well below the critical temperature T_c), the standard-state fugacity is the fugacity of pure liquid 1 at the temperature of the solution and at the constant reference pressure P^r . For supercritical component 2 (the temperature T of the solution is near or above the critical temperature T_c), the standard-state fugacity is its Henry's constant in solvent 1 at the temperature of the solution and at P^r . As a result, both activity coefficients approach unity as the liquid solution becomes infinitely dilute with respect to the light component:

$$\gamma_1^{(P^r)} \rightarrow 1 \quad \text{as } x_1 \rightarrow 1 \quad (21)$$

$$\gamma_2^{*(P^r)} \rightarrow 1 \quad \text{as } x_2 \rightarrow 0 \quad (22)$$

The unsymmetric convention of normalization has the advantage that it avoids the use of any ill-defined hypothetical liquid standard state for the noncondensable supercritical component. It has been repeatedly found that no unique reference fugacity exists for such a hypothetical liquid; for a noncondensable supercritical component, the hypothetical pure-liquid fugacities obtained from vapor-liquid equilibria of that component in various solvents may differ considerably from each other. Ambiguity in the standard-state fugacity of a supercritical gas can be avoided by the use of the well-defined and experimentally accessible Henry's constant (25). $H_{2(1)}^{(P^r)}$ is given by:

$$H_{2(1)}^{(P^r)} = H_{2(1)}^{(P_1^s)} \exp \int_{P_1^s}^{P^r} \frac{\bar{v}_2^\infty}{RT} dP \quad (23)$$

where $H_{2(1)}^{(P_1^s)}$ is evaluated by extrapolating to $x_2 = 0$ a plot of $\ln f_2/x_2$ vs. x_2 . In Equation 23, P_1^s is the saturation (vapor) pressure of solvent 1 and \bar{v}_2^∞ is the liquid partial molar volume of component 2 infinitely dilute in solvent 1.

Excess Gibbs energy. Following Scatchard (39), we define the excess Gibbs energy per mole of solution by

$$\frac{g^{E*}}{RT} = x_1 \ln \gamma_1^{(P^r)} + x_2 \ln \gamma_2^{*(P^r)} \quad (24)$$

Table I. Self-interaction Constants for Some Binary Systems

System	$T, ^\circ R$	$\alpha_{22(1)},$ lb-mole/ ft ³	System	$T, ^\circ R$	$\alpha_{22(1)},$ lb-mole/ ft ³	System	$T, ^\circ R$	$\alpha_{22(1)},$ lb-mole/ ft ³
Methane(2)- ethane(1)	259.7	0.425	Methane(2)- n-pentane(1) contd.	619.7	0.706	Ethane(2)- propane(1)	259.7	0.066
	309.7	0.305		679.7	0.939		309.7	0.059
	359.7	0.182		739.7	1.230		359.7	0.051
	409.7	0.210	Ethylene(2)- ethane(1)	359.7	0.075		409.7	0.043
	459.7	0.333		419.7	0.058		459.7	0.034
Methane(2)- propane(1)	509.7	0.680		459.7	0.039		509.7	0.026
	259.7	0.342		499.7	0.053		559.7	0.025
	309.7	0.322	Ethylene(2)- acetylene(1)	519.7	0.069		579.7	0.029
	359.7	0.322		424.7	0.305		599.7	0.038
	409.7	0.355		459.7	0.270		619.7	0.053
	459.7	0.415		499.7	0.244		639.7	0.099
	491.7	0.462	Ethane(2)- acetylene(1)	424.7	0.538	Propane(2)- n-pentane(1)	559.7	0.023
Methane(2)- n-pentane(1)	509.7	0.498		459.7	0.490		619.7	0.032
	559.7	0.593		499.7	0.365		679.7	0.049
	619.7	0.936		519.7	0.277		739.7	0.080
	559.7	0.548					799.7	0.141

In view of the unsymmetric normalization, g^{E*} vanishes at infinite dilution with respect to component 2 but not with respect to component 1; that is,

$$g^{E*} \rightarrow 0 \quad \text{as} \quad x_2 \rightarrow 0$$

but

$$g^{E*} \neq 0 \quad \text{as} \quad x_1 \rightarrow 0$$

As defined here, the ideal solution ($g^{E*} = 0$) is one where at constant temperature and pressure the fugacity of the light component is given by Henry's law and that of the heavy component by Raoult's law. In molecular terms this means that g^{E*} is zero whenever the concentration of component 2 in the liquid phase is sufficiently small to prevent molecules of component 2 from interacting with one another.

In a manner analogous to that used by Wohl (42), the excess Gibbs energy can be represented by summing interactions of molecules:

$$\frac{g^{E*}}{RT(x_1q_1 + x_2q_2)} = -\alpha_{22(1)}\Phi_2^2 - \dots \quad (26)$$

where Φ is the effective volume fraction

$$\Phi_2 = \frac{x_2q_2}{x_1q_1 + x_2q_2} \quad (27)$$

where q_i is the effective size of molecule i and where $\alpha_{22(1)}$ is the self-interaction constant of molecules 2 in the environment of molecules 1. In Equation 26 only two-body interactions are considered; higher terms are neglected to keep the number of adjustable parameters to a minimum.

Activity coefficients can be found from the exact relations

$$\ln \gamma_1^{(P^r)} = \left(\frac{\partial n_T g^{E*}/RT}{\partial n_1} \right)_{T,P,n_2} \quad (28)$$

$$\ln \gamma_2^{*(P^r)} = \left(\frac{\partial n_T g^{E*}/RT}{\partial n_2} \right)_{T,P,n_1} \quad (29)$$

where n_1 is the number of moles of component 1 and n_T is the total number of moles.

Diluted van Laar model for binary liquid mixtures. Equations 26, 27, and 28 yield the classical van Laar equations (for unsymmetric normalization) as reported previously (25). Muirbrook (20) has shown that these equations, containing two adjustable parameters, are unsatisfactory for describing the properties of some systems which are at a temperature much above the critical temperature of the light component or near the critical temperature of the heavy component. In addition, Muirbrook found that the three-suffix Margules equations were also unsatisfactory (20).

The probable reason for the failure of the classical van Laar treatment is due to van Laar's assumption that q_1 and q_2 are constants independent of composition. The q 's are parameters which reflect the cross sections, or sizes, or spheres of influence of the molecules; at conditions remote from critical, where the liquid molar volumes is close to a linear function of the mole fraction, it is reasonable to assume that the q 's are composition independent. However, for a liquid mixture of a non-condensable component 2 with a subcritical liquid 1, the molar volume of the mixture is a highly nonlinear