Infinite Dilution Fugacity Coefficients and the General Behavior of Dilute Binary Systems

A universally valid formal expression for the composition dependence of solute and solvent fugacity coefficients in any dilute binary system far from criticality is derived in this paper. In the present context, dilution denotes the $y_1 \rightarrow 0$ limit, regardless of the mixture's molar density. The results are independent of the system under study and of the choice of equation of state. The solute fugacity coefficient is simply the product of a composition-independent term (the infinite dilution fugacity coefficient) and an exponential decay composition correction. These two parameters have important thermodynamic implications: their temperature and pressure derivatives are related to the solute's partial molar enthalpy and volume, respectively. When applied to activity coefficients, the same theoretical analysis yields universal relationships for the composition dependence of activity coefficients which can be used as consistency checks for empirical correlations. The relationship between infinite dilution activity and fugacity coefficients can be used to estimate relative solubilities of a given solute in different solvents. Excellent agreement is found when the theoretical expressions are tested with three different binary systems involving a nonvolatile solid solute and a supercritical fluid.

P. G. Debenedetti and S. K. Kumar
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

SCOPE

Fugacity coefficients are important in phase equilibrium calculations via the equation of state approach. They can be obtained from standard thermodynamic expressions by means of a suitable pressure-explicit equation of state. Highly nonlinear expressions result in all cases.

In particular, we have been interested in the fugacity coefficient of a very dilute component. In some ways, this is analogous to the study of infinitely dilute activity coefficients, a concept that has proved of value in modeling liquid solutions. In such cases, the dilute component experiences interactions only with the solvent molecules, and solute-solute effects are essentially absent. The composition dependence of the solute and solvent fugacity coefficients in dilute solutions are found to obey simple and universally valid relationships, which are derived in this paper through purely thermodynamic arguments, with no reference whatsoever to any particular choice of equation of state.

An analysis of such infinitely dilute fugacity coefficients should prove valuable in interpreting data in, say, supercritical extractions where the solute is often present in quite low concentrations.

CONCLUSIONS AND SIGNIFICANCE

The solute fugacity coefficient in dilute binary systems is shown to obey the simple expression $\hat{\phi}_1 = \hat{\phi}_1^\infty \exp(-Ky_1)$, where $\hat{\phi}_1^\infty$ is the infinite dilution fugacity coefficient, K is a function of temperature and pressure, and y_1 is the solute mole fraction. The temperature and pressure dependence of K are related to the composition dependence of the solute partial molar enthalpy

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Correspondence concerning this paper should be addressed to P.G. Debenedetti at the Department of Chemical Engineering, Princeton University, Princeton, NJ 08544.

and volume expansions about their respective infinite dilute limits.

It is shown that the solute activity coefficient in dilute binary systems obeys a formally identical expression, $\gamma_1 = \gamma_1^\infty \exp(-Ky_1)$.

The relationship between infinite dilution activity and fugacity coefficients can be used to estimate relative solubilities of a given solute in different solvents.

Because the treatment foregoes any reference to specific systems or equations of state, the conclusions are completely general, and are in fact found to be valid throughout the entire range from infinite dilution to saturation when tested for several binary systems consisting of a solid solute and a supercritical fluid.

Fugacity Coefficients

The chemical potential, $\hat{\mu}_i$, fugacity, $\hat{f}_i$, and fugacity coefficient, $\hat{\phi}_i$, of a component i ($i = 1, \ldots, n$) in a mixture are related as follows

$$\hat{\mu}_i = RT \ln \hat{f}_i + \lambda_i(T) \tag{1}$$

$$\hat{f}_i = \hat{\phi}_i y_i P \tag{2}$$

where λ_i is a function of temperature, and y_i is the mole fraction of component i.

In the equation of state approach to phase equilibrium calculations, component fugacities in coexisting phases are equated, and the corresponding fugacity coefficients are expressed as a function of temperature, pressure, and mixture composition through an appropriate equation of state.

For a simple n-component mixture and π coexisting phases, there are $(n - 1)\pi + 2$ intensive variables [$\pi(n - 1)$ mole fractions, system temperature, and pressure], $n + 2 - \pi$ of which must be specified a priori, according to the phase rule (Gibbs, 1875). The resulting $n(\pi - 1)$ unknowns must be calculated from a system of $n(\pi - 1)$ equations of the form

$$y_i^{(\alpha)} \hat{\phi}_i^{(\alpha)} = y_i^{(\beta)} \hat{\phi}_i^{(\beta)} \tag{3}$$

where α and β denote different phases. If we consider, as an illustration, an n-component system and two phases, n equations of the form of Eq. 3 must be solved to calculate, for example, $(n - 1)$ mole fractions in the β phase and the system temperature, given the α-phase composition and system pressure.

Fugacity coefficients can be calculated from a suitable pressure-explicit equation of state from the relationship

$$RT \ln \hat{\phi}_i = -\int_\infty^{\underline{V}} \left[\left(\frac{\partial P}{\partial N_i} \right)_{T,\underline{V},N[i]} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \ln Z \tag{4}$$

where underbars denote extensive quantities, $N[i]$ implies constancy of all mole numbers except N_i, and Z is the mixture compressibility factor. The resulting expressions for the composition dependence of $\hat{\phi}_i$ are, in general, highly nonlinear.

For dilute binary mixtures, to which we shall henceforth limit our attention, simple, universal expressions for the solute and solvent fugacity coefficients are derived in this paper. The relations are applicable to all systems far from criticality, and are independent of the equation of state used to model the specific system. The solute fugacity coefficient is shown to be the product of a composition-independent term (the infinite dilution fugacity coefficient) and an exponential decay composition correction. The former represents a new concept with interesting implications; the exponential factor, on the other hand, is related to the system's composition at the limit of stability. The temperature and pressure dependence of the exponential decay factor and of the infinite dilution fugacity coefficient, moreover, are related to the thermal and volumetric properties of the mixture.

Derivation of the Basic Relationships

We consider a dilute binary mixture far from criticality. Let 1 denote the solute and 2 the solvent. We expand the solvent fugacity coefficient about the $y_2 \to 1$ limit, at constant temperature and pressure,

$$\ln \hat{\phi}_2(T, P, y_2) = [\ln \hat{\phi}_2(T, P)]_{y_2 \to 1} + \sum_{n=1}^{\infty} \left[\frac{\partial^n \ln \hat{\phi}_2}{\partial y_2^n} \right]_{T,P,y_2 \to 1} \frac{(y_2 - 1)^n}{n!} \tag{5}$$

and differentiate, to obtain

$$\left[\frac{\partial \ln \hat{\phi}_2}{\partial y_2} \right]_{T,P,} = \sum_{n=1}^{\infty} \left[\frac{\partial^n \ln \hat{\phi}_2}{\partial y_2^n} \right]_{T,P,y_2 \to 1} \frac{(y_2 - 1)^{(n-1)}}{(n - 1)!} \tag{6}$$

or, defining

$$C_n \equiv \left[\frac{\partial^n \ln \hat{\phi}_2}{\partial y_2^n} \right]_{T,P,y_2 \to 1} \tag{7}$$

we rewrite Eq. 6 as

$$\left[\frac{\partial \ln \hat{\phi}}{\partial y_2} \right]_{T,P} = \sum_{n=0}^{\infty} C_{n+1} \frac{(y_2 - 1)^n}{n!} = C_1 - C_2 y_1 + 0(y_1^2) \tag{8}$$

where the coefficients are a function of T and P.

From the Gibbs-Duhem equation, we can write

$$\left[\frac{\partial \ln \hat{\phi}_2}{\partial \ln y_2} \right]_{T,P} = \left[\frac{\partial \ln \hat{\phi}_1}{\partial \ln y_1} \right]_{T,P} \tag{9}$$

which, in the light of Eq. 8 yields

$$\left[\frac{\partial \ln \hat{\phi}_1}{\partial y_1} \right]_{T,P} = \frac{y_2}{y_1} [C_1 - C_2 y_1 + 0(y_1^2)] \tag{10}$$

Since $\ln \hat{\phi}$ can be expanded in series for any finite and nonzero $\hat{\phi}$, all C_n's are finite or zero. For dilute solutions, therefore, we drop quadratic and higher order terms, and integrate from infinite dilution to y_1,

$$\int_{\ln\hat{\phi}_1^\infty}^{\ln\hat{\phi}_1} d\ln\hat{\phi}_1 = \int_0^{y_1}\left(\frac{1-y_1}{y_1}\right)[C_1 - C_2 y_1]\,dy_1 \qquad (11)$$

and obtain

$$\ln\left(\frac{\hat{\phi}_1}{\hat{\phi}_1^\infty}\right) = \left(C_1\ln y_1 - C_1 y_1 - C_2 y_1 + \frac{C_2 y_1^2}{2}\right)\Bigg|_0^{y_1} \qquad (12)$$

where the notation

$$\hat{\phi}_1^\infty = \lim_{y_1\to 0}\hat{\phi}_1(y_1, T, P) \qquad (13)$$

has been used, and will henceforth be called the infinite dilution fugacity coefficient. We now neglect quadratic terms in Eq. 12 (as demanded by the corresponding approximation in Eq. 10) and write

$$C_1 = \left[\frac{\partial\ln\hat{\phi}_2}{\partial y_2}\right]_{T,P,y_2\to 1} = 0 \qquad (14)$$

a fundamental property derived in Appendix A, to obtain

$$\hat{\phi}_1 = \hat{\phi}_1^\infty\exp(-Ky_1) \qquad (15)$$

with

$$K = C_2 = \left[\frac{\partial^2\ln\hat{\phi}_2}{\partial y_2^2}\right]_{T,P,y_2\to 1} \ (\neq 0) \qquad (16)$$

From Eq. 15 we obtain, using Eq. 9, and after integrating from infinite dilution to the actual mixture composition,

$$\hat{\phi}_2 = \hat{\phi}_2^o\exp[-K(\ln y_2 + y_1)] \qquad (17)$$

with

$$\hat{\phi}_2^o = \lim_{y_2\to 1}\hat{\phi}_2(T, P, y_2) \qquad (18)$$

The previous derivations are independent of the equation of state used to model the system of interest. The basic relationships (Eqs. 15 and 18), are therefore valid for all binary systems in the dilute limit and far from criticality.

The thermodynamic implications of K will now be derived. From Eq. 15 we obtain

$$\left[\frac{\partial\ln\hat{\phi}_1}{\partial\ln y_1}\right]_{T,P} = -Ky_1 \qquad (19)$$

For a binary mixture, stability criteria can be expressed in many equivalent ways (Modell and Reid, 1983). In the present case, we choose

$$1 + \left(\frac{\partial\ln\hat{\phi}_1}{\partial\ln y_1}\right)_{T,P} = 0 \qquad (20)$$

At any given temperature and pressure, Eq. 20 can, in principle, be solved for y_1; this represents the solute mole fraction at the mixture's limit of stability (y_{LS}). From Eqs. 19 and 20 we obtain

$$K = \frac{1}{y_{LS}} \qquad (21)$$

whereupon the solute fugacity coefficient reads

$$\hat{\phi}_1 = \hat{\phi}_1^\infty\exp(-y_1/y_{LS}) \qquad (22)$$

and, in addition, because of Eq. 16, we have

$$\left[\frac{\partial^2\ln\hat{\phi}_2}{\partial y_2^2}\right]_{T,P,y_2\to 1} = \frac{1}{y_{LS}} \qquad (23)$$

which suggests an interesting connection between the mixture's behavior at infinite dilution and its limit of stability.

Although the validity of Eq. 21 (and therefore of Eqs. 22 and 23) will be discussed below in connection with the derivative properties of K and $\hat{\phi}_1^\infty$, it follows at once from their derivation that the resulting expressions are valid if and only if the diluteness assumption is realistic up to the mixture's limit of stability. This represents a severe constraint, and we therefore expect Eqs. 21 to 23 to be less general than Eq. 15.

Because y_1 cannot exceed y_{LS}, it follows from Eq. 22 that the compositional variation of $\hat{\phi}_1$ must necessarily fall between the limits 1 and e^{-1}, a conclusion that is of course subject to the same constraints that apply to the relationships used in its derivation.

From general thermodynamic arguments, it has been shown that the solute and solvent fugacity coefficients of all binary systems obey very simple relationships in the dilute limit. The solute fugacity coefficient can then be written as the product of two terms: the infinite dilution fugacity coefficient (which is composition-independent) and an exponential decay composition correction, whose parameter (K) is related to the system's composition at its limit of stability.

We now derive relationships between infinite dilution fugacity coefficients and infinite dilution activity coefficients. An activity coefficient is defined as (Modell and Reid, 1983)

$$\gamma_i(T, P, y_i) = \frac{\hat{f}_i(T, P, y_i)}{y_i\hat{f}_i^+(T, P^+, y_i^+)} \qquad (24)$$

where $\hat{f}_i^+$ is the fugacity of component i at T and reference pressure (P^+) and composition (y_i^+).

$$\gamma_i = \frac{Py_i\hat{\phi}_i}{y_iP^+\hat{\phi}_i^+y_i^+} = \frac{\hat{\phi}_i P}{\hat{\phi}_i^+y_i^+P^+} \qquad (25)$$

and, therefore,

$$\gamma_1^\infty = \frac{\hat{\phi}_1^\infty P}{\hat{\phi}_1^+y_1^+P^+};\quad \gamma_2^o = \frac{\hat{\phi}_2^o P}{\hat{\phi}_2^+y_2^+P^+} \qquad (26)$$

or, in other words,

$$\frac{\gamma_1}{\gamma_1^\infty} = \frac{\hat{\phi}_1}{\hat{\phi}_1^\infty};\quad \frac{\gamma_2}{\gamma_2^o} = \frac{\hat{\phi}_2}{\hat{\phi}_2^o} \qquad (27)$$

This is an identity, and is valid for all choices of $\hat{f}_i^{+}$. From Eqs. 27, 15, and 17, we obtain

$$\gamma_1 = \gamma_1^{\infty} e^{-Ky_1} \tag{28}$$

$$\gamma_2 = \gamma_2^{0} e^{-K(\ln y_2 + y_1)} \tag{29}$$

where the superscripts ∞ and 0 denote the $y_1 \rightarrow 0$ limit as applied to solute and solvent, respectively.

Therefore, all dilute binary systems must obey Eqs. 28 and 29. It follows from Eq. 28 that the limiting slope of $\ln \gamma_1$ is related to K through

$$-K(T, P) = \left(\frac{\partial \ln \gamma_1}{\partial y_1}\right)_{T,P,y_2 \rightarrow 1} \tag{30}$$

Furthermore, in the dilute limit we can expand the exponential and neglect quadratic terms, to obtain

$$\gamma_1 = \gamma_1^{\infty}(1 - Ky_1) \tag{31}$$

which imposes a linear composition dependence upon γ_1 as $y_1 \rightarrow 0$.

Examples

To test the practical usefulness and applicability of the expressions derived in the previous section, we consider phase equilibrium between a solid solute and a supercritical fluid under conditions where a classical treatment is valid (i.e., away from any critical point). The extent of the narrow critical region where classical approaches fail has been discussed elsewhere (Sengers and Levelt-Sengers, 1983). Binary supercritical systems have attracted considerable interest (Kurnik et al., 1981; Johnston et al., 1982; Krukonis et al., 1984), since they constitute the simplest (and hence the most theoretically tractable) case of multicomponent phase equilibrium involving a supercritical fluid.

For these systems it is customary to assume a pure, incompressible condensed phase; if, in addition, the pressure is much greater than the solute's vapor pressure, the equilibrium solubility of the solute in the supercritical fluid is given by (Prausnitz, 1965)

$$y_1^{(eq)} = \frac{P_{vp}}{P} \cdot \frac{1}{\hat{\phi}_1} \cdot \exp\left(\frac{PV_1^s}{RT}\right) \tag{32}$$

where P_{vp} is the solute's vapor pressure and V_1^s its molar volume in the condensed phase. The righthand side, then, is the product of three terms: the ideal gas solubility (P_{vp}/P, which by itself predicts a solubility that is inversely proportional to pressure at any given temperature), the inverse solute fugacity coefficient, and an exponential correction which, at the pressures of interest (<500 bar; 50 MPa) is typically less than 10. The ratio of actual to ideal gas solubility (i.e., Py_1/P_{vp}) is called the enhancement factor.

The essential features of the $y_1^{(eq)}$ vs. T and P relationship [solubility minima (Kurnik et al., 1981), solubility maxima (Kurnik and Reid, 1981), enhancement factors of order 10^6 (Schmitt and Reid, 1985)] are therefore contained in the $\hat{\phi}_1^{-1}$ term.

Fugacity coefficients are normally obtained from a pressure-explicit equation of state, using Eq. 4. As an example, we consider cubic equations of state, which in their most general form can be written as (Schmidt and Wenzel, 1980)

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + uVb + wb^2} \tag{33}$$

where u and w are numbers that characterize the particular equation of state being used. When the mixture a and b parameters are obtained from pure component parameters through the following mixing rules,

$$b = \sum_{i=1}^{n} b_i y_i \tag{34}$$

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} y_i y_j \tag{35}$$

the expression for $\hat{\phi}_i$ reads

$$\ln \hat{\phi}_i = \frac{bi}{b}(Z - 1) - \ln(Z - B) + \frac{A}{B\sqrt{u^2 - 4w}}\left[\frac{2\sum_k y_k a_{ik}}{a} - \frac{b_i}{b}\right] \cdot \ln \frac{Z + B\left(\frac{u - \sqrt{u^2 - 4w}}{2}\right)}{Z + B\left(\frac{u + \sqrt{u^2 - 4w}}{2}\right)} \tag{36}$$

with

$$A = aP/(RT)^2 \tag{37}$$

$$B = bP/RT \tag{38}$$

The composition dependence of $\hat{\phi}_i$ follows from Eqs. 34, 35, 37, and 38, and from the implicit y-dependence of Z. Other equations of state or mixing rules can, of course, be used. The approach is not predictive, and it necessitates the introduction of at least one adjustable parameter. The latter is generally a binary interaction coefficient (k_{ij}), which is ordinarily defined through a combining rule,

$$a_{ij} = (a_i a_j)^{1/2}[1 - k_{ij}(1 - \delta_{ij})] \tag{39}$$

(δ_{ij} is Kronecker's delta), and regressed from experimental data by minimizing a suitable objective function—in the present case, $\Sigma\,|\log[y_1(k_{ij})/y_1(\exp)]|$ where $y_1(\exp)$ is the experimentally measured equilibrium solubility. Binary interaction coefficient regressions are usually made in temperature-dependent fashion (i.e., one k_{ij} per isotherm).

The following references were used in Figures 1 to 5 to regress binary interaction parameters from experimental data: CO_2-benzoic acid (Schmitt, 1984); SF_6-naphthalene (Debenedetti, 1984); CO_2-acridine (Schmitt, 1984); CO_2-phenanthrene (Kurnik, 1981).

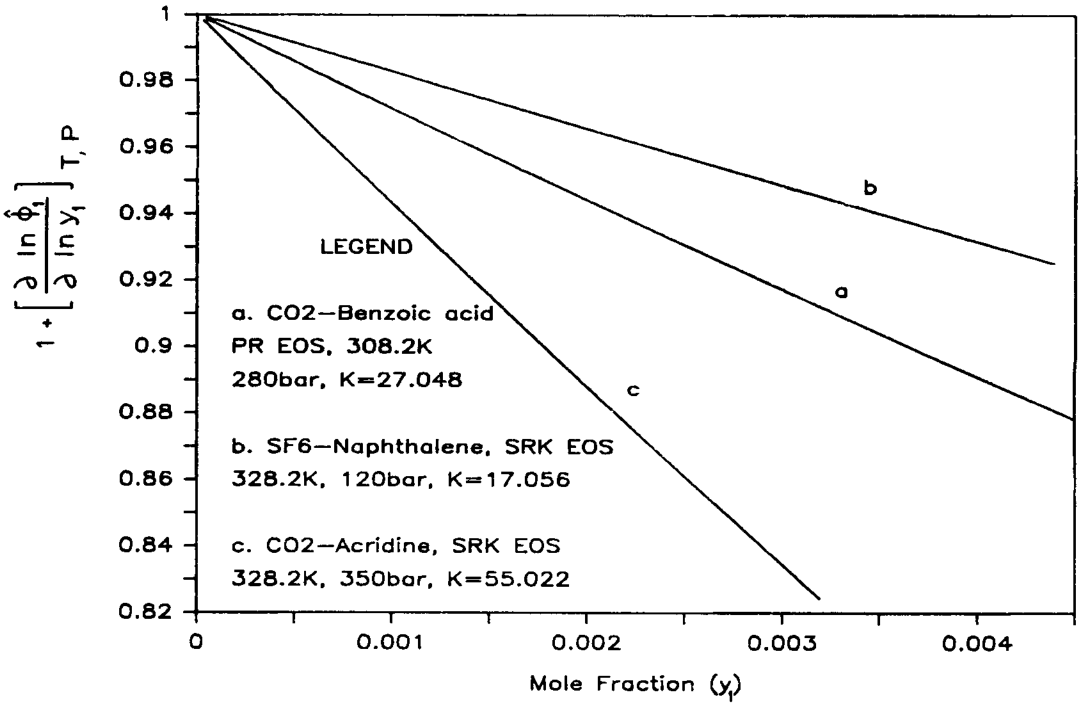

Figure 1. $1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}$ vs. y_1 relationship for different systems.

From Eq. 19 it follows that, for dilute systems, a plot of the quantity $1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}$ vs. solute mole fraction should yield a straight line of slope $-K$ and unit ordinate-intercept. Differentiating Eq. 36, and after considerable algebraic manipulation, a complicated expression for the quantity $1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)$ results (Debenedetti, 1984). Figure 1 is a plot of the calculated values of this quantity vs. solute mole fraction, from infinite dilution to saturation, for different binary systems involving a solid solute and a supercritical fluid, and two cubic equations of state (Soave-Redlich-Kwong and Peng-Robinson).

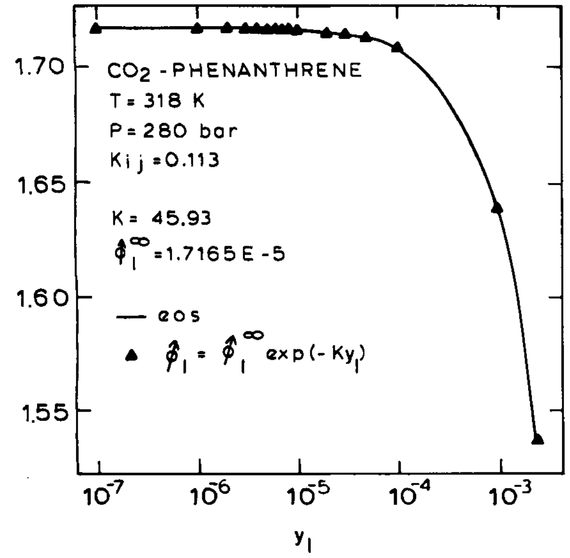

Figure 2. Comparison of Peng-Robinson prediction for $\hat{\phi}_1$ with Eq. 15.

The predicted linearity is exhibited in all cases. This is remarkable since the simplicity of this relationship is not at all evident in the full expression for $[1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}]$. Figure 1 shows only examples of a behavior that was observed whenever a binary system consisting of a solid solute and a supercritical fluid was investigated. Because Eq. 15 is a universal dilute limit, whenever a binary system exhibits low equilibrium solubilities (as is typically the case with solid-supercritical fluid equilibria), then the exponential decay expression constitutes an accurate representation of the fugacity coefficient from infinite dilution to saturation.

From the calculated values of the $[1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}]$ vs. y_1 line, a value of K can be obtained by least-squares regression. Furthermore, $\hat{\phi}_1$ follows from Eq. 36, and hence $\hat{\phi}_1^\infty$ follows from its operational definition (Eq. 13). Figure 2 is a comparison of the equation of state prediction for $\hat{\phi}_1$, in the CO_2-phenanthrene system (line) with the corresponding values predicted by Eq. 15 (triangles), with K and $\hat{\phi}_1^\infty$ obtained as explained above. The same comparison is shown in Figure 3 for the benzoic acid-CO_2 system on a linear solute mole fraction scale. At saturation the difference between the equation of state prediction and Eq. 15 is only 0.35%.

It follows from the nature of the arguments used in the derivation of Eq. 15 that this is a general formal relationship, valid for all dilute binary systems. Equation 15, however, is not predictive: this can be seen from the way in which K and $\hat{\phi}_1^\infty$ were obtained in the previous examples. The usefulness of an expression such as Eq. 15, however, lies in the fact that both K and $\hat{\phi}_1^\infty$ represent concepts with interesting thermodynamic implications and significance, as will be shown below.

In the first place, $\hat{\phi}_1^\infty$ is, by definition, composition-independent; because the exponential correction is a number of order 1, it follows from Eq. 32 that the behavior of the system at infinite dilution (i.e., $\hat{\phi}_1^\infty$) is of fundamental importance in determining

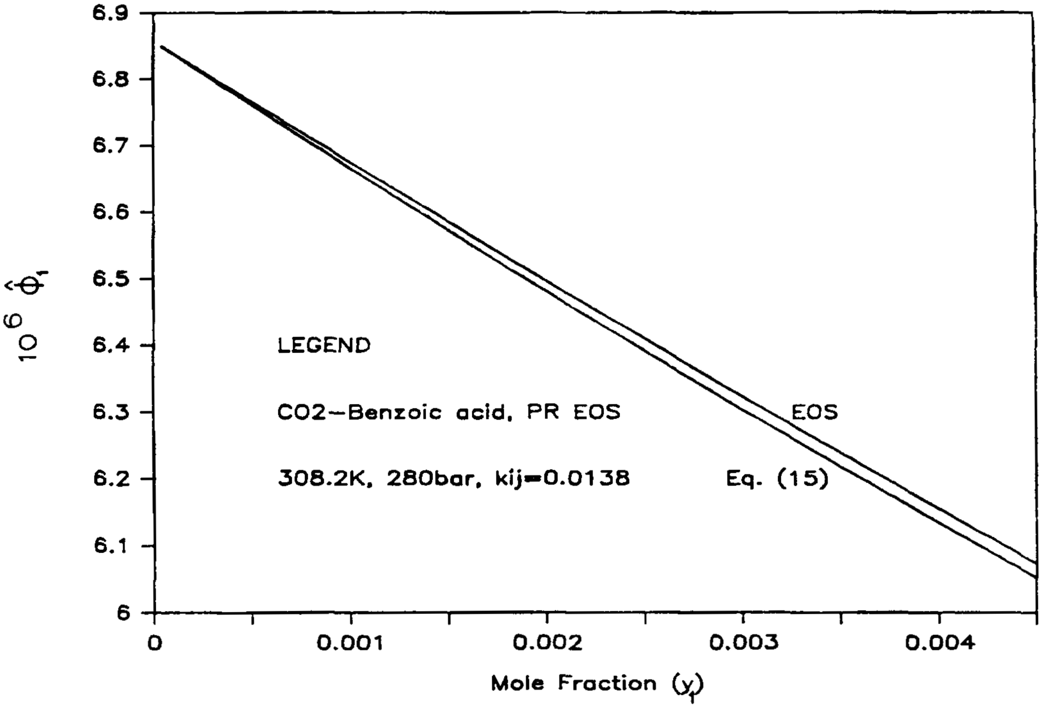

Figure 3. Comparison of Peng-Robinson prediction for $\hat{\phi}_1$ with Eq. 15.

the equilibrium solubility of the solute in the supercritical fluid. A quantity that is independent of composition, furthermore, should be amenable to a group contribution interpretation.

We now return to Eqs. 26 and 27. If the reference composition (ie., y_i^+) is taken as unity, we can write, for a given P^+

$$\frac{\gamma_1^\infty(I)}{\gamma_1^\infty(II)} = \frac{\hat{\phi}_1^\infty(I)}{\hat{\phi}_1^\infty(II)} \tag{40}$$

where *I and II* denote different solvents. Because exp $(-Ky_1)$ is of order one, it follows that Eq. 40 can be used to estimate a priori relative solubilities of a given solute in different solvents at given T and P. This is so because infinite dilution activity coefficients can be estimated readily by group contribution methods such as UNIFAC (Reid et al., 1977).

Derivative Properties

In order to derive expressions for the temperature and pressure dependence of K and $\hat{\phi}_1^\infty$, we first write the relationships

$$\left[\frac{\partial(\bar{G}_i/T)}{\partial T}\right]_{P,y_i} = -\frac{\bar{H}_i}{T^2} \tag{41}$$

$$\left[\frac{\partial \bar{G}_i}{\partial P}\right]_{T,y_i} = \bar{V}_i \tag{42}$$

whereupon, from Eq. 1 we obtain

$$\left[\frac{\partial \ln \hat{\phi}_i}{\partial T}\right]_{P,y_i} = -\frac{1}{R}\left\{\frac{\bar{H}_i}{T^2} + \frac{d[\lambda_i(T)/T]}{dT}\right\} = -\frac{1}{RT^2}[\bar{H}_i - H_i^*] \tag{43}$$

where H_i^* is the ith component's ideal-gas enthalpy, and

$$\left[\frac{\partial \ln \hat{\phi}_i}{\partial P}\right]_{T,y_i} = \frac{\bar{V}_i}{RT} - \frac{1}{P} \tag{44}$$

But, from Eq. 15 we can write, for dilute systems,

$$\left(\frac{\partial \ln \hat{\phi}_1}{\partial T}\right)_{P,y_1} = \left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial T}\right)_P - y_1\left(\frac{\partial K}{\partial T}\right)_P \tag{45}$$

$$\left(\frac{\partial \ln \hat{\phi}_1}{\partial P}\right)_{T,y_1} = \left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial P}\right)_T - y_1\left(\frac{\partial K}{\partial P}\right)_T \tag{46}$$

so that

$$\left(\frac{\partial K}{\partial T}\right)_P = \frac{\bar{H}_1 - \bar{H}_1^\infty}{y_1 RT^2} \tag{47}$$

$$\left(\frac{\partial K}{\partial P}\right)_T = -\frac{\bar{V}_1 - \bar{V}_1^\infty}{y_1 RT} \tag{48}$$

In addition, if we consider Eqs. 43 and 44 at infinite dilution, we can write

$$\left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\bar{H}_1^\infty}{T^2} + \frac{d}{dT}(\lambda_1(T)/T)\right] = -\frac{1}{RT^2}[\bar{H}_1^\infty - H_1^*] \tag{49}$$

$$\left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial P}\right)_T = \frac{\bar{V}_1^\infty}{RT} - \frac{1}{P} \tag{50}$$

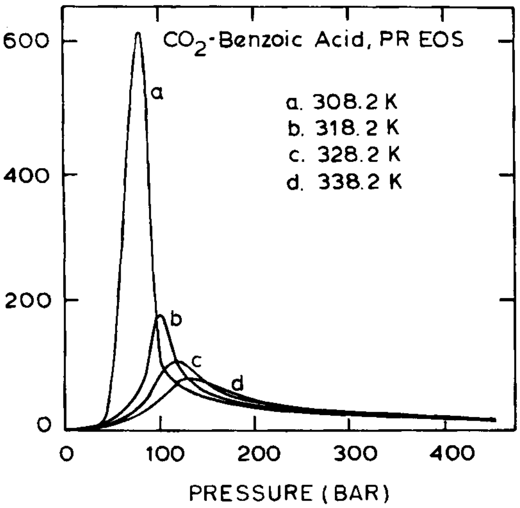

Figure 4. Dependence of K upon pressure, at four different temperatures.

CO$_2$-benzoic acid; Peng-Robinson equation; $T = 308.2\ K$, $k_{ij} = 0.0138$; $T = 318.2\ K$, $k_{ij} = 0.010308$; $T = 328.2\ K$, $k_{ij} = -0.003336$; $T = 338.2K$, $k_{ij} = -0.01172$.

From Eqs. 47 and 48 and the fact that K is independent of y_1, we conclude that the righthand side numerators must be linear in y_1. This has already been derived (Krichevskii, in Rozen, 1976), in connection wih the general properties of partial molar property expansions about the infinitely dilute limit. (See Appendix B for a derivation of these expansions and their asymmetric behavior.) Here we state the final result,

$$\bar{B}_1 = \bar{B}_1^{\infty} + \alpha y_1 + \text{higher order terms} \tag{51}$$

$$\bar{B}_2 = B - \frac{\alpha y_1^2}{2} + \text{higher order terms} \tag{52}$$

where $\bar{B}_i$ is a generic partial molar property, B a pure solvent molar property, and $\bar{B}_1^{\infty}$ and α are composition-independent (but T- and P-dependent) quantities.

Figure 4 is a plot of K vs. pressure, at various temperatures, for the CO$_2$-benzoic acid system. In order to interpret the curves, we write (Eq. 48)

$$\left(\frac{\partial K}{\partial P}\right)_T = -\frac{1}{RT}\left[\alpha(T,P) + \beta(T,P)\frac{y_1}{2} + \cdots\right] \tag{53}$$

where β is the quadratic coefficient in the solute expansion (Eq. 51). At any given temperature, α is negative at low pressures, and positive at high pressures. When $(\partial K/\partial P)_T$ vanishes, the solute partial molar volume is independent of composition, and this implies the vanishing of all of the coefficients in Eq. 51.

The coefficients α and β have an important implication. We first write

$$RT\ln\hat{\phi}_1 = \int_0^P \left[\bar{V}_1 - \frac{RT}{P}\right] dP \tag{54}$$

which follows from Eq. 1 and its ideal gas mixture limit (Denbigh, 1981)

$$\hat{\mu}_i^{IG} = \bar{G}_i^{IG} = RT\ln Py_i + \lambda_i(T) \tag{55}$$

and differentiate to obtain

$$RT\left(\frac{\partial \ln\hat{\phi}_1}{\partial y_1}\right)_{T,P} = \int_0^P \left(\frac{\partial \bar{V}_1}{\partial y_1}\right)_{T,P} dP \tag{56}$$

Next, we use the expansion of $\bar{V}_1$ about $\bar{V}_1^{\infty}$ (Eq. 51)

$$RT\left(\frac{\partial \ln\hat{\phi}_1}{\partial y_1}\right)_{T,P} = \int_0^P [\alpha(T,P) + \beta(T,P)y_1 + \cdots]\, dP \tag{57}$$

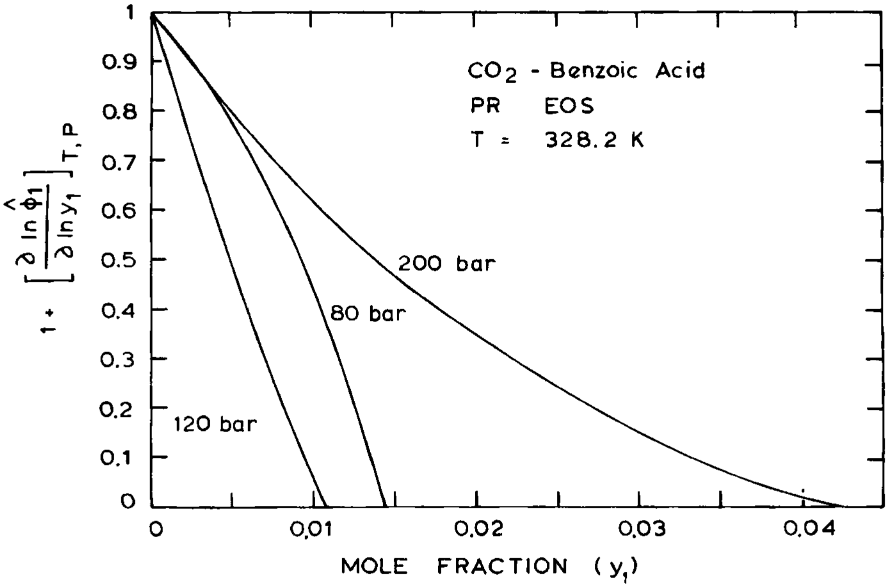

Figure 5. $1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}$ **for CO$_2$-benzoic acid from infinite dilution to the predicted limit of stability.**

which can be rewritten as

$$RT\left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P} = \langle \alpha(T,P)\rangle P + y_1 \langle \beta(T,P)\rangle P + \cdots \tag{58}$$

where $\langle\ \rangle$ implies an average over the pressure range 0 to P.

However, from Eq. 15 we can write

$$\left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P} = -K \tag{59}$$

We can therefore conclude that the criterion for the validity of Eq. 15, or, in other words, the dilute limit assumption, is

$$y_1 \ll \left|\frac{\langle \alpha(T,P)\rangle}{\langle \beta(T,P)\rangle}\right| \tag{60}$$

Although a plot such as Figure 4 can provide useful information about α, nothing can be said about β. We simply note that if, at any given temperature, the pressure dependence of β is such that $\langle \beta(T,P)\rangle$ vanishes, i.e.,

$$\langle \beta(T,P)\rangle = \frac{1}{P}\int_0^P \beta(T,P)dP = 0 \tag{61}$$

then Eq. 15 is valid even beyond $y_1^{(eq)}$.

Because Eq. 15 was obtained from a truncated series expansion, it is always possible to preserve its form and note that, when the dilute limit assumption breaks down, K becomes composition-dependent. This can be seen in Figure 5, which was obtained by calculating the function $1 + (\partial \ln \hat{\phi}_1/\partial \ln y_1)_{T,P}$ from infinite dilution to the limit of stability for the benzoic acid-CO_2 system, at 328.2 K and three different pressures, with the Peng-Robinson equation of state. If Eq. 15 is strictly valid (i.e., with K composition-independent) throughout the full $0 \leq y_1 \leq y_{LS}$ range, then the curves in Figure 5 would be straight lines, and, therefore, the relationship

$$K = \frac{1}{y_{LS}} \tag{21}$$

would be exact. In Table 1, the equation of state predictions for y_{LS} corresponding to Figure 5 are compared with the corresponding K^{-1} values.

From Table 1 and Figure 5 we conclude that, in general, the dilute limit assumption cannot be rigorously used up to the limit of stability. The good agreement between K^{-1} and y_{LS} at 120 bar (12 MPa) implies that, for this system, Eq. 61 is satisfied in the vicinity of 328.2 K and 120 bar.

Table 1. Test of the $K = y_{LS}^{-1}$ Relationship: CO_2-benzoic acid; $T = 328.2$ K; Peng-Robinson Equation of State

P bar	y_{LS}	K^{-1}	ϵ %
80	1.434×10^{-2}	2.607×10^{-2}	81.8
120	1.067×10^{-2}	9.450×10^{-3}	11.4
200	4.217×10^{-2}	2.338×10^{-2}	−44.6

SI conversion: kPa = bar × 100.

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Notation

a = attractive parameter in cubic equation of state, ML^5t^{-2} mol^{-2}
b = repulsive parameter in cubic equation of state, $L^3 \cdot$ mol^{-1}
B = generic molar property, Eqs. 51 and 52
C_n = expansion coefficient, Eq. 7
f_i = fugacity of component i in a mixture, $ML^{-1}t^{-2}$
G = molar Gibbs energy, ML^2t^{-2}mol^{-1}
H = molar enthalpy, ML^2t^{-2}mol^{-1}
K = exponential decay factor
k_{ij} = binary interaction coefficient
N_i = mole number of component i, mol
P = pressure, $ML^{-1}t^{-2}$
P_{vp} = vapor pressure, $ML^{-1}t^{-2}$
R = universal gas constant, ML^2t^{-2}mol$^{-1}T^{-1}$
T = absolute temperature, K
v = algebraic constant in cubic equation of state
V = molar volume, L^3mol^{-1}
$\underline{V}$ = volume, L^3
w = algebraic constant in cubic equation of state
y_i = mole fraction of ith component in a mixture
Z = compressibility factor ($=P\underline{V}/NRT$)

Greek letters

α = coefficient in generic partial molar expansion
β = coefficient in generic partial molar expansion
γ = coefficient in generic partial molar expansion
δ = coefficient in generic partial molar expansion
ϵ = coefficient in generic partial molar expansion
γ_i = activity coefficient of ith component in a mixture
λ_i = temperature-dependent constant for component i, ML^2t^{-2} mol^{-1}
$\hat{\mu}_i$ = chemical potential of ith component in a mixture, ML^2t^{-2} mol^{-1}
$\hat{\phi}_i$ = fugacity coefficient of ith component in a mixture

Superscripts

IG = ideal gas mixture
S = solid
α = α phase
β = β phase
o = solvent at the $y_1 \rightarrow 0$ limit
∞ = solute at the $y_1 \rightarrow 0$ limit
$+$ = reference conditions
$\hat{\ }$ = value of a property in solution
$-$ = partial molar property

Subscripts

1 = solute; first-order constant in Eq. 7
2 = solvent; second-order constant in Eq. 7
i = ith component in a mixture
j = jth component in a mixture
$\_$ = total (extensive) property

Appendix A: Proof of Eq. 14

To prove the identity expressed in Eq. 14:

$$C_1 = \left[\frac{\partial \ln \hat{\phi}_2}{\partial y_2}\right]_{T,P,y_2 \rightarrow 1} = 0$$

we first expand $\ln \hat{\phi}_1$ and $\ln \hat{\phi}_2$ in terms of y_1, at constant T and P

$$\ln \hat{\phi}_1 = \ln \hat{\phi}_1^\infty + y_1 \left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P,y_1\to 0} + \frac{y_1^2}{2}\left(\frac{\partial^2 \ln \hat{\phi}_1}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots \tag{A1}$$

$$\ln \hat{\phi}_2 = \ln \hat{\phi}_2^\infty + y_1 \left(\frac{\partial \ln \hat{\phi}_2}{\partial y_1}\right)_{T,P,y_1\to 0} + \frac{y_1^2}{2}\left(\frac{\partial^2 \ln \hat{\phi}_2}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots \tag{A2}$$

and differentiate to obtain

$$\left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P} = \left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P,y_1\to 0} + y_1\left(\frac{\partial^2 \ln \hat{\phi}_1}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots \tag{A3}$$

$$\left(\frac{\partial \ln \hat{\phi}_2}{\partial y_2}\right)_{T,P} = -\left[\left(\frac{\partial \ln \hat{\phi}_2}{\partial y_1}\right)_{T,P,y_1\to 0} + y_1\left(\frac{\partial^2 \ln \hat{\phi}_2}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots\right] \tag{A4}$$

We now invoke Eq. 9, an identity which follows from the Gibbs-Duhem equation, and write

$$(y_1 - 1)\left(\frac{\partial \ln \hat{\phi}_2}{\partial y_1}\right)_{T,P,y_1\to 0} + y_1(y_1 - 1)\left(\frac{\partial^2 \ln \hat{\phi}_2}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots = y_1\left(\frac{\partial \ln \hat{\phi}_1}{\partial y_1}\right)_{T,P,y_1\to 0} + y_1^2\left(\frac{\partial^2 \ln \hat{\phi}_1}{\partial y_1^2}\right)_{T,P,y_1\to 0} + \cdots \tag{A5}$$

This expression must hold for all values of y_1. From the $y_1 \to 0$ limit, we immediately obtain

$$\left(\frac{\partial \ln \hat{\phi}_2}{\partial y_2}\right)_{T,P,y_1\to 0} = C_1 = 0 \tag{A6}$$

Appendix B: Partial Molar Expansions

We rederive here results originally obtained elsewhere (Krichevskii, in Rozen, 1976) and used in the present paper, Eqs. 51 and 52. We first expand any partial molar property in terms of y_1, at constant T and P

$$\bar{B}_1 = \bar{B}_1^\infty + \alpha y_1 + \frac{\beta}{2} y_1^2 + \cdots \tag{B1}$$

$$\bar{B}_2 = B + \gamma y_1 + \frac{\delta}{2} y_1^2 + \frac{\epsilon}{3} y_l^3 + \cdots \tag{B2}$$

where

$$\alpha = \alpha(T, P) = \left(\frac{\partial \bar{B}_1}{\partial y_1}\right)_{T,P,y_1\to 0} \tag{B3}$$

$$\beta = \beta(T, P) = \left(\frac{\partial^2 \bar{B}_1}{\partial y_1^2}\right)_{T,P,y_1\to 0} \tag{B4}$$

and analogous definitions for γ and δ. Note that, as $y_1 \to 0$, $\bar{B}_1$ approaches $\bar{B}_1^\infty$ and $\bar{B}_2$ approaches the pure solvent molar property. Expansions such as Eqs. B1 and B2 are valid away from criticality (Rozen, 1976).

We now write the Gibbs-Duhem equation,

$$\left(\frac{\partial \bar{B}_1}{\partial \ln y_1}\right)_{T,P} = \left(\frac{\partial \bar{B}_2}{\partial \ln y_2}\right)_{T,P} \tag{B5}$$

and apply this to Eqs. B1 and B2,

$$y_1 (\alpha + \beta y_1 + \cdots) = (y_1 - 1)(\gamma + \delta \gamma_1 + \epsilon y_1^2 + \cdots) \tag{B6}$$

which can be rearranged as follows,

$$\alpha y_1 + \beta y_1^2 + \cdots = -\gamma + y_1(\gamma - \delta) + y_1^2(\delta - \epsilon) + \cdots$$

Because the Gibbs-Duhem equation must be satisfied identically, we must have

$$\gamma = 0 \tag{B7}$$

(which follows from letting $y_1 \to 0$), and

$$\alpha = -\delta \tag{B8}$$

whereupon we can rewrite Eqs. B1 and B2

$$\bar{B}_1 = \bar{B}_1^\infty + \alpha\, y_1 + \text{higher order terms} \tag{B9}$$

$$\bar{B}_2 = B - \frac{\alpha\, y_1^2}{2} + \text{higher order terms} \tag{B10}$$

We note that this derivation is formally identical to the procedure used in Appendix A. In fact, Eqs. B9 and B10 are not restricted to partial molar properties but are valid for the expansion of any composition-dependent property in a binary system for which the infinite dilution limits are defined, and which satisfies a Gibbs-Duhem relation. Thus, we can write

$$\ln \hat{\phi}_1 = \ln \hat{\phi}_1^\infty + \alpha'' y_1 + \text{higher order terms} \tag{B11}$$

$$\ln \hat{\phi}_2 = \ln \hat{\phi}_2^o - \frac{\alpha'' y_1^2}{2} + \text{higher order terms} \tag{B12}$$

where $\hat{\phi}_2^o$ is defined in Eq. 18.

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