Limiting vs. Apparent Critical Behavior of Henry's Constants and *K* Factors

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At low and moderate pressures, Henry's constant k_H is the fundamental quantity for describing the solubility of gases in liquids. Japas and Levelt Sengers (1989) derived an asymptotic relationship for the variation of k_H in the neighborhood of the solvent's critical point. This relationship may be expressed as

$$T \ln (k_H/f_1^s) = A + B(\rho_{L,1}^s - \rho_{c,1}) \qquad (1)$$

where T is the absolute temperature, f_1^s and $\rho_{L,1}^s$ are the fugacity and liquid-phase density of the solvent at saturation, $\rho_{c,1}$ is the solvent's critical density, and A and B are constants. A similar asymptotic relationship exists for the infinite-dilution limit of the vapor-liquid partition coefficient (K factor):

$$T \ln K^\infty = 2B(\rho_{L,1}^s - \rho_{c,1}) \qquad (2)$$

where $K^\infty = \lim_{x_2, y_2 \to 0} (y_2/x_2)$, y_2 and x_2 are the vapor and liquid mole fractions of the solute, and B is the same constant appearing in Eq. 1.

Harvey and Levelt Sengers (1990) showed that, when Henry's-constant data for nonpolar gases in water are plotted in the manner suggested by Eq. 1, straight lines are obtained over a wide range of conditions. The linear region extends from temperatures as low as 100°C to the highest temperatures at which data exist (approximately 10 K below water's critical point for some solutes). Similar results have been obtained for several nonaqueous systems (Japas and Levelt Sengers, 1989; Harvey and Levelt Sengers, 1990). Harvey and Levelt Sengers (1990) used Eq. 1 as the basis for a successful three-parameter correlation of aqueous Henry's constants covering the entire range of temperatures from 0°C to water's critical point.

The extraordinary linearity of the data when plotted on the coordinates of Eq. 1 led us to assume that the slopes of these lines were equal to their asymptotic values. Further analysis, in part involving Eq. 2 and in part involving comparison with mixture critical lines, has shown that that assumption is incorrect and that Eq. 1 attains its asymptotic slope only in a small region closer to the critical point than the extent of the data. In the following, we show the analysis leading to this conclusion and suggest that a better estimate for the asymptotic value of B is provided by Eq. 2.

Analysis

Equation 1 states that, along the path going down the solvent's saturation curve from its critical point, the quantity $T \ln (k_H/f_1^s)$ is linear with respect to the saturated-liquid density $\rho_{L,1}^s$. Because of symmetry about the critical point, an equally valid linear asymptotic relationship is obtained with the saturated-vapor density $\rho_{v,1}^s$, or with combinations such as $(\rho_{L,1}^s - \rho_{v,1}^s)$. Furthermore, since a linear variation in density is asymptotically equivalent to a linear variation in volume, one could just as easily use volumetric quantities such as $V_{L,1}^s$ or $(V_{v,1}^s - V_{L,1}^s)$. In the previous work, all of these quantities were tried as the independent variable in plots of $T \ln (k_H/f_1^s)$ and only $\rho_{L,1}^s$ gave linear behavior over an extensive region. The same multitude of potential linear relationships exists for the quantity $T \ln K^\infty$; again $\rho_{L,1}^s$ provides much better linearity than the other choices. We mention this to illustrate that the linearity exhibited by experimental data when plotted according to Eqs. 1 and 2 is exceptional, with the more "common" condition being substantial departure from linearity for other choices of the independent variable.

It is, of course, not a certainty that a line of the form (of Eq. 1 or 2), which passes through experimental data, will be the asymptotic line. One way in which such lines may be checked for consistency is to plot data for the same system according to Eqs. 1 and 2; if these lines are truly asymptotic, their slopes must differ by a factor of two. Figures 1 and 2 show such plots for

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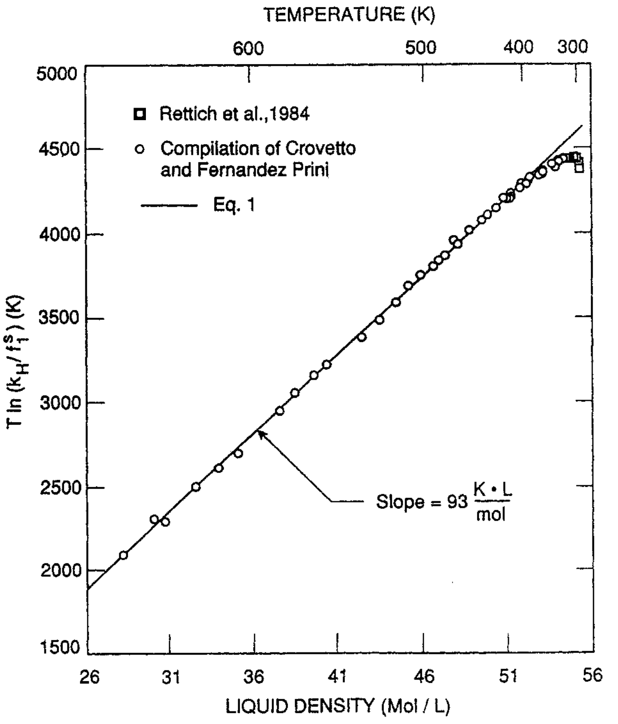

Figure 1. Linear relationship of $T \ln (k_H/f_1^s)$ vs. $\rho^s_{L,1}$ for N_2 in H_2O.

The critical density of H_2O is 17.87 mol/L.

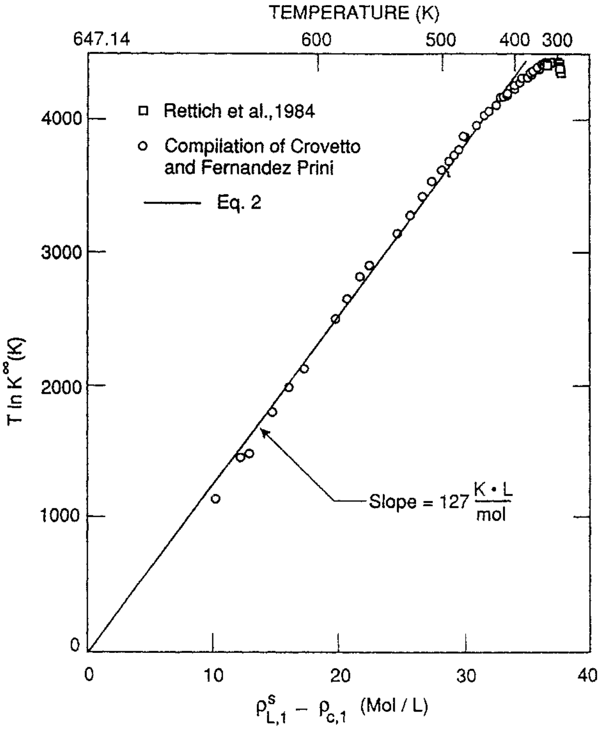

Figure 2. Linear relationship of $T \ln K^\infty$ vs. $(\rho^s_{L,1} - \rho_{c,1})$ for N_2 in H_2O.

nitrogen in water; Henry's-constant data were taken from a recent compilation of aqueous Henry's constants by Fernández Prini and Crovetto (1989; personal communications, 1989) and, at low temperatures, from Rettich et al. (1984). The conversion from Henry's constants to infinite-dilution K factors requires vapor-phase fugacity coefficients at infinite dilution; these were computed with the same equation of state (Peng and Robinson, 1976) used in preparing the Henry's-constant compilation. The K factors were not corrected for liquid-phase nonideality at the (finite-concentration) experimental conditions; an approximate correction for this effect (Alvarez and Fernandez Prini, in press) brings the highest-temperature points into better agreement with the line in Figure 2. The ratio of the slopes is approximately 1.4 instead of the required two. The inescapable conclusion from this comparison is that one of the lines (or possibly both) is not asymptotic.

Figures 3 and 4 show the same comparison for methane in propane. The Henry's constants in Figure 3 were compiled by Chueh and Prausnitz (1968). [These constants were given at a reference pressure of zero. Conversion of the values to saturation pressure, as required in Eq. 1, was performed using infinite-dilution partial molar volumes computed by the method of Chueh and Prausnitz (1967).] The infinite-dilution K factors in Figure 4 were obtained from vapor-liquid equilibrium data in the literature (Reamer et al., 1950; Wichterle and Kobayashi, 1972). For this system as well, both plots are linear but the slopes do not differ by the necessary factor of two.

Similar comparisons yield similar results for the CO/benzene system used as an example by Japas and Levelt Sengers (1989) and for other aqueous systems considered in the Henry's constant work of Harvey and Levelt Sengers (1990). Clearly at least one of these two methods of examining the data produces a nonasymptotic slope; the challenge is to determine which is the likely culprit.

One clue is provided by a feature of the K factor expression. Equation 2 contains no constant analogous to A in Eq. 1. Because the vapor and liquid phases become identical at the solvent's critical point, the value of K^∞ at that point is required to be unity. This means that K factor plots such as those in Figures 2 and 4 must go to the origin. The fact that the lines established by the data in these figures extrapolate well to the origin is strong evidence that these lines are asymptotic or nearly so. A crossover to a different asymptotic slope would require two inflections in the curve between the last data point and the origin; while this is not impossible, it seems unlikely. In contrast, the value of the ordinate at $\rho^s_{L,1} = \rho_{c,1}$ is not known *a priori* in Figures 1 and 3, so it would be quite reasonable for these curves to turn upward and attain a different asymptotic slope.

Additional evidence comes from examination of mixture critical lines. The quantity B in Eqs. 1 and 2 can be related to the composition dependence of the total pressure at the critical point:

$$(\partial P/\partial x)^c_{V,T} = R\rho^2_{c,1}B \tag{3}$$

where R is the molar gas constant and superscript c indicates a derivative evaluated at the solvent's critical point. This derivative is ubiquitous in dilute-mixture thermodynamics; among other things it is related to the limiting slope of the solvent's vapor pressure curve and to the initial departure of the critical

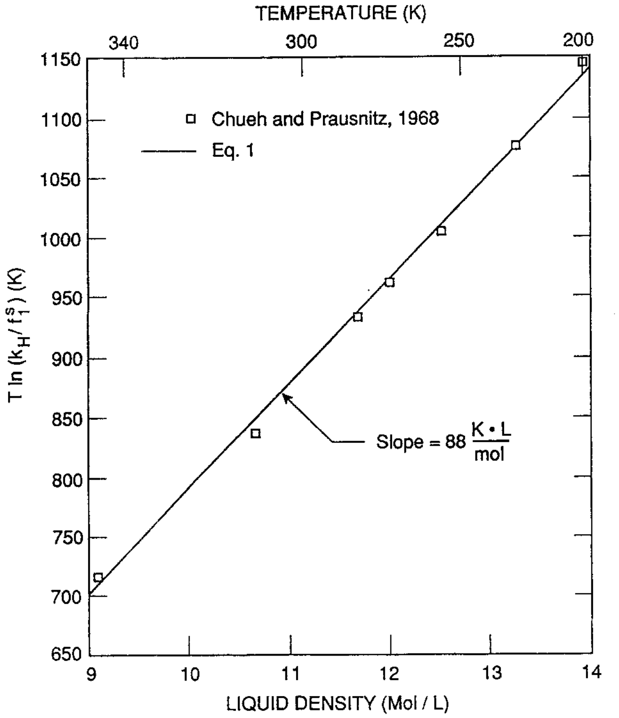

Figure 3. Linear relationship of $T \ln (k_H/f_1^s)$ vs. $\rho^s_{L,1}$ for CH_4 in C_3H_8.

The critical density of C_3H_8 is 5.0 mol/L.

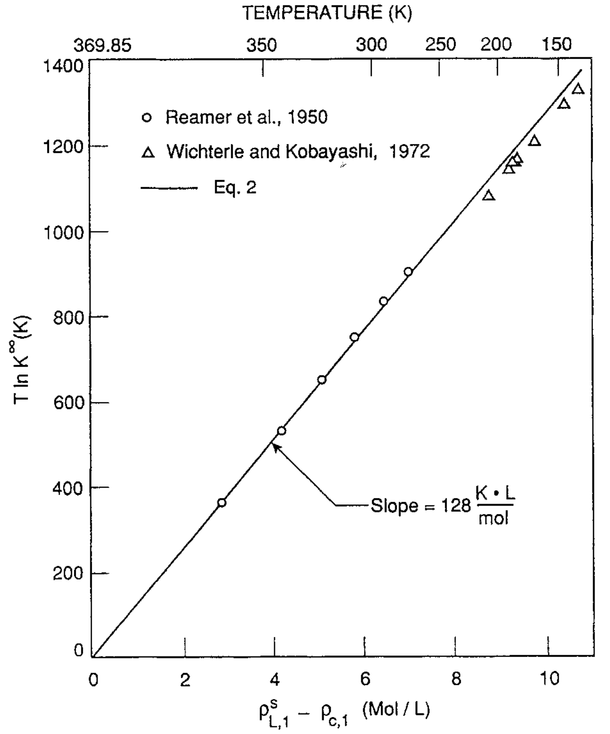

Figure 4. Linear relationship of $T \ln K^\infty$ vs. $(\rho^s_{L,1} - \rho_{c,1})$ for CH_4 in C_3H_8.

line from the critical point (Krichevskii, 1967; Chang et al., 1984):

$$(\partial P/\partial x)^c_{V,T} = dP/dx|^c_{CRL} - [dP/dT|^c_\sigma][dT/dx|^c_{CRL}] \qquad (4)$$

where subscript σ indicates a derivative taken in the direction of the solvent's vapor pressure curve and subscript CRL indicates that the derivative is taken along the critical line.

We now have three independent ways of computing $(\partial P/\partial x)^c_{V,T}$: from Henry's constants using Eqs. 1 and 3; from K factors using Eqs. 2 and 3; and (for systems where these data have been measured) from critical lines via Eq. 4. Table 1 shows values of $(\partial P/\partial x)^c_{V,T}$ computed in these three ways for six systems. In each case, the value determined from K factors is more consistent with the experimental critical-line data. The values in the first two columns are precise to within approximately ±1 in the last digit. Systematic error from the equation of state used to model vapor-phase nonideality (which would not be unexpected for aqueous systems) was ruled out by trying several different equations of state and by including a well-understood nonpolar system. While the experimental difficulties of determining critical lines are such that computations from Eq. 4 are subject to considerable uncertainty, consistent trends in Table 1 indicate strongly that the Henry's-constant plots do not give the true asymptote and that the K factor plots are at least much closer to being asymptotic.

Discussion

The reasons for the lengthy linear regions obtained from Eq. 1, as shown in Figures 1 and 3, are still unknown. Since these regions are not asymptotic, we must attribute this behavior for the most part to a fortuitous combination of nonasymptotic effects. Even in the case of Eq. 2, where it appears that the correct asymptotic slope is determined by the data, the range of linearity is sufficiently great that (especially in light of the nonlinearity when equally asymptotic independent variables other than $\rho^s_{L,1}$ are used) some serendipity must be involved. Regardless of the reasons, the experimental results make it clear that Eqs. 1 and 2 provide very useful sets of coordinates on which to plot experimental data.

Our analysis has shown that the Henry's-constant correlation (Harvey and Levelt Sengers, 1990) based on the linearity of Eq. 1 is not as firmly based in theory as was originally believed. The usefulness of the correlation, however, is not significantly diminished; it still provides an excellent fit to data with one fewer parameter than existing correlations. Furthermore, the large linear region, fortuitous though it may be, still provides a

Table 1. Values of $(\partial P/\partial x)^c_{V,T}$ (in GPa) Calculated from Henry's Constants (Eqs. 1 and 3), K Factors (Eqs. 2 and 3), and Critical Lines (Eq. 4)

System	From k_H	From K^∞	From Critical Line	Ref. for Critical Line
H_2—H_2O	0.22	0.16	0.15	Seward and Franck (1981)
Ar—H_2O	0.20	0.16	0.13	Wu et al. (1990)
N_2—H_2O	0.25	0.17	0.18	Japas and Franck (1985a)
O_2—H_2O	0.22	0.16	0.14	Japas and Franck (1985b)
CO_2—H_2O	0.18	0.12	0.10	Tödheide and Franck (1963)
CH_4—C_3H_8	0.018	0.013	0.012	Reamer et al. (1950)

reliable basis for extrapolation of data to high temperatures as long as one avoids the last few degrees before the critical point.

If one were concerned with Henry's constants very near the critical temperature, the problems with the nonasymptotic behavior of Eq. 1 could be circumvented by converting the Henry's constants to infinite-dilution K factors (or working with K factors from the beginning), extrapolating K factors with Eq. 2, and converting the resulting values back to Henry's constants. This requires a fugacity-coefficient model, but such a model is required anyway when Henry's constants or infinite-dilution K factors are extracted from experimental solubility data.

Finally, we mention that this work resolves the apparent discrepancy noted earlier (Harvey and Levelt Sengers, 1990) between values of $(\partial P/\partial x)^c_{V,T}$ determined from Henry's constants and those determined from critical-line slopes via Eq. 4. The discrepancy is not (as had been conjectured) the fault of the critical-line slopes. Instead, as shown by Table 1, it appears to be due to the nonasymptotic results obtained from the Henry's constant plots; slopes obtained from K factors are reasonably consistent with the experimental critical lines. This consistency, along with the agreement of Eq. 2 with the necessary limit when extrapolated to the critical density, suggests that Eq. 2 provides a good estimate of the true asymptotic slope.

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Notation

A = intercept in Eq. 1
B = slope in Eq. 1
f = fugacity
k_H = Henry's constant
K^∞ = K factor (partition coefficient) at infinite dilution
P = total pressure
R = molar gas constant
T = absolute temperature
V = molar volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Greek letters

ρ = molar density

Subscripts

1 = component 1 (solvent)
2 = component 2 (solute)
c = value at critical point
CRL = derivative evaluated along critical line
L = liquid phase
v = vapor phase
σ = derivative evaluated along saturation curve

Superscripts

c = value of derivative at solvent critical point
s = evaluated on solvent saturation curve

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