Gas Solubility and Henry's Law Near the Solvent's Critical Point

It has been experimentally observed, for water and nonaqueous solvents alike, that Henry's constant passes through a maximum and then declines as the temperature is raised from the triple point to the critical point. From classical and nonclassical models, we derive exact relations for the value of Henry's constant and its temperature dependence at the solvent's critical point, showing that the decline of this constant is a universal phenomenon. We demonstrate that the limiting temperature dependence of Henry's constant can be predicted from the thermodynamic properties of the pure solvent and the initial slope of the critical line. The validity of our prediction is tested by comparing it with experimental solubility data for several gases in high-temperature water and benzene. Our predictive model appears valid over a temperature range of at least 15% in temperature below the critical point of the solvent.

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Introduction

A number of recent publications (Beutier and Renon, 1978; Schotte, 1985) have drawn attention to the fact that while gas solubility data in low-temperature water abound, high-temperature data, although important for industrial, power (Crovetto et al., 1982), and geological (Potter and Clynne, 1978; Kishima and Sakai, 1984) applications, are scarce. Moreover, extrapolation of low-temperature behavior to higher temperatures is uncertain because gas solubilities pass through a minimum and then increase as the temperature rises (Prausnitz and Lichtenthaler, 1986); conversely, Henry's constant values, after an initial rise, pass through a maximum followed by a steep decline in the last few hundred K before the critical point is reached, Figure 1. This phenomenon has also been noted in nonaqueous solvents. Several recent papers have recognized the phenomenon as a universal feature of near-critical solvents and have spent considerable effort at finding an explanation (Beutier and Renon, 1978; Schotte, 1985). There appears to be a consensus that the temperature derivative of Henry's constant should diverge, but neither the value of the critical exponent associated with the divergence, nor its amplitude have been derived. In a recent paper, Levelt Sengers (1989) derived the critical exponent on the basis of a classical (van der Waals or mean-field type) equation of state.

In the present paper, we derive the critical exponent and critical amplitude for this divergence for both classical and nonclassical models. In addition, we present a general thermodynamic argument relating the temperature derivatives of Henry's constant to pure-solvent properties of known divergence. Our result is very simple: the temperature derivative of the logarithm of Henry's constant diverges as the temperature derivative of the solvent's saturated liquid volume, while the amplitude of the divergence can be calculated from the initial slopes of the critical line. In a number of cases where accurate solubility data are available in high-temperature water and benzene we show that our predictions are valid. Several recent papers have made predictions for the behavior of Henry's constant that differ from ours. We show that the differences result from problems the authors experienced with defining the appropriate paths in differentiation and in the taking of limits. In conclusion, we present a rigorous result for the value of Henry's constant and its temperature derivative at the solvent's critical point. We present a phenomenological correlation of this constant and the solvent's density that appears to hold over more than 100 K in both water and benzene. Consequently, the Henry's law limit of solubility has been firmly established in a region that is difficult to have access to experimentally.

Henry's Constant

Although the original definition of Henry's constant was in the context of Henry's law, which related the partial pressure of a gas over a liquid to the amount of gas dissolved, a more general

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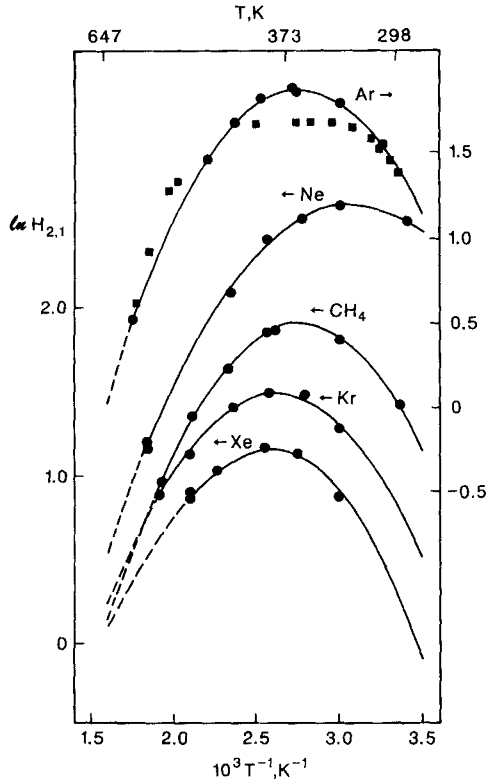

Figure 1. Henry's constant for noble gases in H_2O (Crovetto et al., 1982) vs. 1,000/T in K^{-1}.

Top scale: 647 K = critical point; 373 K = boiling point H_2O; 298 K = 25°C point

definition of Henry's constant has come into use; see, for instance, Prausnitz and Lichtenthaler (1986). This definition pertains to one-phase states and defines Henry's constant as the infinite-dilution limit of the ratio of the fugacity of the solute to its mole fraction. The constant so defined is clearly a function of two variables, T and P. The partial derivatives of this constant are then proportional to the infinite-dilution partial molar volume and enthalpy. At the solvent's critical point, these partial molar properties, and therefore also the partial derivatives, diverge strongly, the precise value of the critical exponent depending on the path of approach in a well-known fashion (Wheeler, 1972; Chang et al., 1984; Levelt Sengers, 1989). We discuss this point in more detail in the Conclusions section.

This paper, however, pertains to the original intent of Henry's law, the limiting behavior of a solute in a two-phase state. We will therefore not use the above generalized definition of Henry's constant.

Henry's Law

In defining Henry's law, we consider a two-component, two-phase system. The least volatile component is called the solvent and is denoted with the subscript 1. The more volatile component, the gas in whose solubility we are interested, is called the solute and is denoted with subscript 2. The fugacities of the two components are f_1, f_2, respectively, and both fugacities are, in principle, functions of pressure, temperature, and composition. The mole fraction of the solute in the liquid phase is denoted by x, and that in the vapor phase by y. Henry's constant $H_{2,1}$ for the volatile solute 2 in solvent 1 is defined as

$$H_{2,1}(T) = \lim_{x\to 0} \{f_2(p, T, y)/x\} \tag{1}$$

where p is the pressure. It should be realized that since two phases are present, there are two degrees of freedom at finite x; therefore, the path to be followed in taking $x \to 0$ is not uniquely defined. In general, one would expect that the limit defined in Eq. 1 would be independent of the path. Near a critical point, however, this cannot be taken for granted. We will, therefore, take the limit in Eq. 1 while keeping the temperature constant. Once the limit is taken, the final state is that of coexisting vapor and liquid of the pure solvent. Consequently, $H_{2,1}$ is a function of only one variable, the temperature (or the pressure).

We will find it useful to consider the fugacity coefficients ϕ_1, ϕ_2 of the two components. They are defined in the vapor phase, as

$$\phi_1(P, T, y) = f_1(p, T, y)/\{(1 - y)p\} \tag{2}$$

$$\phi_2(P, T, y) = f_2(p, T, y)/\{yp\} \tag{3}$$

Consequently, from Eqs. 1–3, we have

$$H_{2,1}(T_1) = p_\sigma(T_1) \lim_{\substack{x\to 0\\ T\to T_1}} \phi_2(p, T_1, y) \lim_{\substack{x\to 0\\ T\to T_1}} (y/x) \tag{4}$$

Here $p_\sigma(T_1)$ is the saturation vapor pressure of the pure solvent at T_1. We will denote the infinite-dilution value of ϕ_2 by ϕ_2^∞. We have been allowed to set the limit of the product equal to the product of the limits because, as we will show, $\lim_{x\to 0}(y/x)$ and $\lim_{x\to 0} \phi_2$ are well behaved and finite at all T, the former equaling unity at the solvent's critical point. Since $y = x$ at a critical point, expression 4, under the assumption that $\lim \phi_2$ exists at T_c, leads directly to the result noted by Beutier and Renon (1978):

$$H_{2,1}(T_c) = p_c\phi_2^{\infty c} \tag{5}$$

where $\phi_2^{\infty c}$ denotes the limiting value of ϕ_2^∞ at the solvent's critical point. It is important to convince oneself that this limit exists. The relation

$$\ln \phi_2(p_1, T_1, y) = \int_0^{p_1} \left[\frac{\bar{V}_2}{RT_1} - \frac{1}{p}\right] dp \tag{6}$$

where $\bar{V}_2$ is the partial molar volume of the vapor phase, gives reason for caution, since it is well known that $\bar{V}_2$ diverges strongly at the solvent's critical point (Wheeler, 1972; Chang et al., 1984). By substituting

$$\bar{V}_2 = V - (1 - y) \frac{(\partial p/\partial y)_{VT_1}}{(\partial p/\partial V)_{yT_1}} \tag{7}$$

where V is the molar volume of the solution, into Eq. 6, we obtain

$$\ln \phi_2(p_1, T_1, y) = \int_0^{p_1} \left[\frac{V}{RT} - \frac{1}{p}\right] dp + (1 - y) \int_\infty^{V_1} - \frac{(\partial p/\partial y)}{RT} dV \tag{8}$$

where $V_1 = V_1(p_1, T_1)$. If the limit $y \rightarrow 0$ is taken, the first integral results in $\ln \phi_1^*$ of the pure solvent at T_1, a well-defined finite value even at $T = T_c$. Since $p = -(\partial A/\partial V)_{T_1,y}$, the second integral results in $(\partial A^r/\partial y)_{y\rightarrow 0,T_1,V_1}$, where A^r is the residual Helmholtz free energy; its y derivative, at $y = 0$, is well defined and finite even at T_c (appendix A). We will denote it as $A_y^{r\infty}$. Consequently, $\ln \phi_2$ exists for all T including T_c:

$$\ln \phi_2^\infty(T_1) = \ln \phi_1^*(T) + A_y^{r\infty}/RT \qquad (9)$$

Thus, Henry's constant exists at the solvent's critical point and is generally nonzero, contrary to the statement of Potter and Clynne (1978). An alternative expression for $H_{2,1}$ that we will find convenient for our purpose is

$$\ln (H_{2,1}/f_1^*) = A_y^{r\infty}/RT + \lim_{y\rightarrow 0} \ln (y/x) \qquad (10)$$

Eq. 10 follows from Eq. 4, with Eqs. 2, 3, and 9.

Temperature Dependence of Henry's Constant—Classical Treatment

The next question regards the behavior of $d \ln H_{2,1}/dT$ when $T \rightarrow T_c$. Well-known expressions relating temperature and pressure derivatives of Henry's constant to infinite-dilution partial molar enthalpies and volumes, which are known to diverge strongly, might lead one to expect a γ-type divergence (Griffiths and Wheeler, 1970) for $d \ln H_{2,1}/dT$. This, however, is incorrect.

Let us first obtain the limiting behavior of the temperature dependence of $\lim_{x\rightarrow 0}(y/x)$. For a classical Helmholtz free energy, which can be expanded at the solvent's critical point, equality of chemical potentials in coexisting vapor v and liquid l phases leads to the following asymptotic relation:

$$RT \ln (y/x) = -(\partial^2 A/\partial V \partial x)^c [\delta V_v - \delta V_l] + 0(x - y) + \cdots \qquad (11)$$

with $\delta V = V - V_c$. Subscripts c and superscripts c both refer to values calculated at the solvent's critical point. The first term on the righthand side of Eq. 11 is the dominant term when y, x are small. For T below T_c, δV_v and δV_l have opposite sign, so that the bracket remains finite as $x, y \rightarrow 0$. At the critical point, y and x can be used interchangeably. In the limit $y \rightarrow 0$, δV_v, δV_l refer to pure-solvent coexisting volumes. Moreover, in a classical expansion of the chemical potentials at the solvent's critical point (Levelt Sengers, 1989), $\ln \phi_1$ is found to vary as $(\delta V_v)^3$ whereas $\partial A^r/\partial y$ varies as δV_v and therefore dominates the behavior of $\ln \phi_2$. We obtain

$$RT \ln \phi_2^\infty = RT \ln \phi_1^* + (\partial A^r/\partial x)^c + (\partial^2 A^r/\partial V \partial x)^c \delta V_v^* + 0(T - T_c) + \cdots \qquad (12)$$

The superscript ∞ refers to infinite dilution, the superscript * to the pure solvent. Derivatives with superscript c are evaluated at the solvent's critical point, that is, at infinite dilution. In order to simplify notation, we will not explicitly use the symbols ∞, * in that case. Along the coexistence curve, δV_v^* varies as $|T - T_c|^{1/2}$ and therefore the term in δV_v^* in Eq. 12 dominates the term linear in $T - T_c$. From Eqs. 4, and 9–12 we obtain

$$RT \ln H_{2,1} = RT \ln f_1^* + (\partial A^r/\partial x)^c + (\partial^2 A^r/\partial V \partial x)^c \delta V_l^* + \cdots \qquad (13)$$

In the classical case, δV_l^* varies as $|T - T_c|^{1/2}$ along the coexistence curve and therefore $\partial \ln H_{2,1}/\partial T$ diverges as $|T - T_c|^{-1/2}$. Since δV_l^*, being negative, increases to zero on approaching the critical point, and $(\partial^2 A/\partial V \partial x)^c = (-\partial p/\partial x)_{VT}^c$ is negative for a volatile solute, it is seen that $d \ln H_{2,1}/dT$ is negative, so that Henry's constant decreases on approaching the critical point. The classical model thus predicts that $RT \ln (H_{2,1}/f_1^*)$ correlates linearly with the liquid volume. Since this is strictly an asymptotic result, an asymptotically linear correlation

$$\mathrm{RT} \ln (H_{2,1}/f_1^*) = (\partial A^r/\partial y)^c - \frac{1}{\rho_c^2} (\partial^2 A^r/\partial V \partial x)^c \delta \rho_l^* \qquad (14)$$

with $\delta \rho_l = \rho_l - \rho_c$, is likewise expected with the liquid density. The coefficient of the linear relation of $\rho_c^2\, RT \ln (H_{2,1}/f_1^*)$ to the density is predicted to equal $(\partial^2 A/\partial V \partial x)^c$ which, in turn, has been shown to be equal to (Chang et al., 1984):

$$(\partial p/\partial x)_{VT}^c \equiv -(\partial^2 A^r/\partial V \partial x)^c = dp/dx|_{CRL}^c - (dp/dT|_\sigma^c)(dT/dx|_{CRL}^c) \qquad (15)$$

where the derivatives with subscript CRL refer to the initial slope of the critical line and $dp/dT|_\sigma^c$ is the critical value of the slope of the pure solvent's vapor pressure curve.

Temperature Dependence of Henry's Constant—Nonclassical Treatment

The classical treatment of the temperature dependence of $H_{2,1}$ was based on Eq. 4 and resulted from considering the limiting behavior of $\ln \phi_2$ and $\ln (y/x)$. It was found that both properties correlate with the pure-solvent coexistence volume or density, and that their sum has an asymptotically linear dependence on the solvent's liquid volume or density.

The nonclassical treatment follows a similar path. It starts with the alternative expression, Eq. 10, and uses the Leung-Griffiths (1973) model to establish the asymptotic behavior of A_y^r and y/x. The derivation is given in appendix B, and the result is an expression identical to Eq. 14. Since, nonclassically, the density departure $\delta \rho_l$ varies as $|T - T_c|^\beta$, with $\beta = 0.325$, the temperature derivative of $\ln H_{2,1}$ must diverge as $|T - T_c|^{\beta - 1}$; the exponent equals -0.675 for the nonclassical case, to be compared with -0.5 for the classical case.

Thermodynamic Argument

The thermodynamic argument is based on the exact relation, Eq. 10, which we rewrite as follows

$$RT \ln (H_{2,1}/f_1^*) = \lim_{y\rightarrow 0} A_y^r + RT \lim_{y\rightarrow 0} \ln (y/x) \qquad (16)$$

The chemical potential difference $\mu_2 - \mu_1 = \Delta$ is equal in coexistent phases. It equals the composition derivative of the Helmholtz free energy. In terms of the residual Helmholtz free energy A^r, we thus have, in coexisting phases of composition y (vapor) and x (liquid):

$$A_y^r + RT \ln \{y/(1-y)\} = A_x^r + RT \ln \{x/(1-x)\} \tag{17}$$

and therefore

$$\lim_{y \to 0} RT \ln (y/x) = A_x^{r\infty} - A_y^{r\infty} \tag{18}$$

Thus we find

$$RT \ln (H_{2,1}/f_1^*) = A_x^{r\infty} \tag{19}$$

We obtain $(d/dT)(\ln H_{2,1})|_\sigma$ in two steps. First, we obtain the temperature derivative of the righthand side of Eq. 19. Then, we demonstrate that the temperature derivative of f_1^* contributes no further significant anomalies. Thus, from Eq. 19,

$$\frac{d}{dT}(A_x^{r\infty})|_\sigma = \left(\frac{\partial}{\partial T} A_x^{r\infty}\right)_V + \left(\frac{\partial}{\partial V} A_x^{r\infty}\right)_T \frac{dV_l^*}{dT}\bigg|_\sigma \tag{20}$$

The temperature derivative $(\partial/\partial T\, A_x^{r\infty})_V$ can be rewritten as

$$\left(\frac{\partial}{\partial T} A_x^{r\infty}\right)_V = -\lim_{x \to 0} \left(\frac{\partial S^r}{\partial x}\right)_{VT} \tag{21}$$

$(\partial S^r/\partial x)_{VT}$ is a property that remains finite at the critical line and is well-behaved for $x \to 0$ (appendix A). The volume derivative $((\partial/\partial V)\, A_x^{r\infty})_T$ can be rewritten as

$$\left(\frac{\partial}{\partial V} A_x^{r\infty}\right)_T = -\lim_{x \to 0} \left(\frac{\partial p}{\partial x}\right)_{VT} \tag{22}$$

$(\partial p/\partial x)_{VT}$ is a property that, at worst (nonclassically), goes weakly to zero at the critical line, and is finite and well behaved in the limit $x \to 0$ (Griffiths and Wheeler, 1970; appendix A, this paper). Consequently, the behavior of the temperature derivative of $H_{2,1}/f_1^*$ is dominated by the last term in Eq. 20, since dV_l^*/dT diverges to $+\infty$ as $|T - T_c|^{\beta-1}$. Finally, we need to demonstrate that $d \ln f_1^*/dT$ does not contribute a divergence as strong as or stronger than $\beta - 1$. We find

$$\begin{aligned}\frac{d}{dT} \ln f_1^*|_\sigma &= \left(\frac{\partial}{\partial T} \ln f_1^*\right)_P + \left(\frac{\partial}{\partial p} \ln f_1^*\right)_T \frac{dp}{dT}\bigg|_\sigma \\ &= \frac{H_1^0 - H_1^*}{RT^2} + \frac{V_1^*}{RT}\frac{dp}{dT}\bigg|_\sigma \end{aligned} \tag{23}$$

where H_1^0 is the standard state for enthalpy of the pure solvent at T. Since all quantities H_1^*, H_1^0, V_1^*, and $dp/dT|_\sigma$ are finite, the derivative $d \ln f_1^*/dT|_\sigma$ is finite, which completes the proof that $d \ln H_{2,1}/dT_\sigma$ diverges with the exponent $\beta - 1$. Finally, we remark that asymptotically near the critical point, Eq. 20 behaves as

$$A_x^{r\infty} = C_1 - \left(\frac{\partial p}{\partial x}\right)_{VT}^c V_l \tag{24}$$

where C_1 is an undetermined constant. Therefore, for T near T_c,

$$RT \ln (H_{2,1}/f_1^*) = C_1 - \left(\frac{\partial p}{\partial x}\right)_{VT}^c V_l \tag{25}$$

The derivative $(\partial p/\partial x)_{VT}^c = -(\partial^2 A^r/\partial V \partial x)^c$ can be expressed in terms of the critical-line slopes, as shown in Eq. 15.

Since for volatile solutes $(\partial p/\partial x)_{VT}^c > 0$, and since V_l decreases as the temperature drops, $RT \ln (H_{2,1}/f_1^*)$ will increase as the temperature falls below T_c.

Solubility and Partition Coefficient

Beutier and Renon (1978) defined the solubility S_{21} as (in our notation):

$$S_{21} = \lim_{x \to 0} (x/py) \tag{26}$$

The advantage of this definition is that it connects more directly with measurable entities, the total pressure p and the ratio of mole fractions in coexisting phases, than does Henry's constant. It is not difficult to obtain the asymptotic behavior of the temperature derivative of S_{21}. From the relation in Eq. 4 we obtain

$$\ln S_{21}^{-1} = \ln (H_{2,1}/\phi_2^\infty) \tag{27}$$

which relates the solubility S_{21} to quantities of which we have established the asymptotic behavior. Since the asymptotic behavior of $\ln \phi_2^\infty$ is dominated by that of $A_y^{r\infty}/RT$, Eq. 9, and the behavior of $H_{2,1}$ by that of $A_x^{r\infty}/RT$, Eq. 19, the temperature derivative of $\ln S_{21}^{-1}$ will behave as

$$\frac{d\, RT \ln S_{21}^{-1}}{dT}\bigg|_\sigma = \frac{d}{dT}(A_x^{r\infty} - A_y^{r\infty}) \tag{28}$$

which has the same exponent but twice the amplitude of the divergence of $d\, RT\, (\ln H_{2,1}/f_1^*)\, dT$. The inverse of the solubility S_{21} thus declines as the critical point is approached, which means that the solubility increases strongly. The critical value of S_{21}^{-1}, from the definition of Eq. 26, obviously equals p_c.

Another useful quantity in the thermodynamics of solutions is the partition coefficient or K factor. It is defined as

$$K = y/x \tag{29}$$

In the infinite-dilution limit

$$K^\infty = \lim_{x \to 0} y/x = S_{21}^{-1}\, p \tag{30}$$

The critical value of K^∞ is unity and its temperature derivative diverges as that of S_{21}^{-1}, with an exponent of $\beta - 1$. Just as $H_{2,1}/f_1^*$ and S_{21}, K^∞ is expected to correlate asymptotically with the density of the pure solvent.

Comparison with Experiment

Rather than comparing the predicted temperature dependence of $H_{2,1}$ with experiment, we find it more useful to test the predicted linear relation between $T \ln (H_{2,1}/f_1^*)$ and the liquid density. In addition, we compare the experimental slope with the

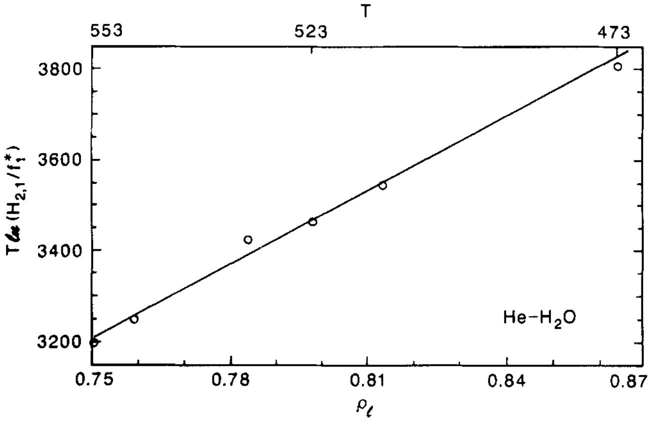

Figure 2. Henry's constant for He in H_2O: $T \ln (H_{21}/f_1^*)$ in K vs. pure-water liquid density ρ_1 in kg · dm^{-3}.

Top scale: corresponding temperatures, K
O Data from Crovetto and Fernandez-Prini (1988); within the scatter they can be represented by a straight line

one predicted from our theory. Crovetto et al. (1982), and Japas and Franck (1985) measured the solubility of several gases in high-temperature water. For properties of pure H_2O, we use the so-called HGK equation (Haar et al., 1984). We have selected the data on the systems He, H_2, and CH_4 in H_2O from the critical evaluation of Crovetto and Fernândez-Prini (1988), where several sources have been taken into account. For the N_2-H_2O system, we used the data of Japas and Franck. In all these cases, a number of data points were available in the range where Henry's constant started to decline. Appendix C gives some details on the treatment of the experimental data and the reliability of the resulting Henry's constant values.

We have tried several pairs of variables, such as $\ln H_{2,1}$ vs. $\rho_l - \rho_v$, $\ln H_{2,1}$ vs. V_v, and so on. The largest-range linear relation is obtained by plotting $T \ln H_{2,1}/f_1^*$ vs. ρ_l. In Figures 2–5 we display these plots. At the top, we show the corresponding temperatures. We observe linearity of the plot over a range of more than 150 K below the steam critical point of 647 K. That this result is not just a happy coincidence for aqueous solutions is demonstrated in Figure 6, where we have made a similar plot for the system CO in benzene (Connolly and Kandalic, 1984). A similar large asymptotic range is found. In Figures 7 and 8, we correlate the data for the K factor and the solubility for the system CO in benzene with the pure-solvent liquid density. The result for the K factor is as good as that for Henry's constant, but the plot for the solubility shows appreciable curvature. This is unavoidable, since the factor p in the definition, Eq. 26, does not vary linearly with ρ_l. In Table 1, we compare the slope of the plot, as predicted from the initial slopes of the critical line—Eqs. 14, 15—with the observed values of Figures 3–5. Given the inherent inaccuracies of the critical-line slopes, we think our results are very good. Although our model cannot predict the absolute value of $H_{2,1}/f_1^*$, it provides a safe guide for extrapolation to T_c if data at lower temperatures are available.

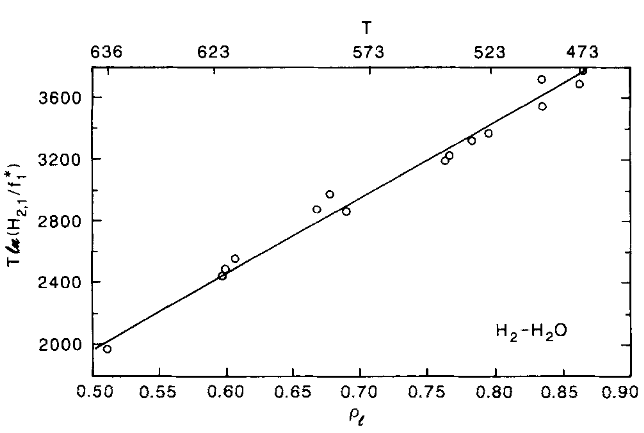

Figure 3. Henry's constant for H_2 in water.

Same convention as in Figure 2

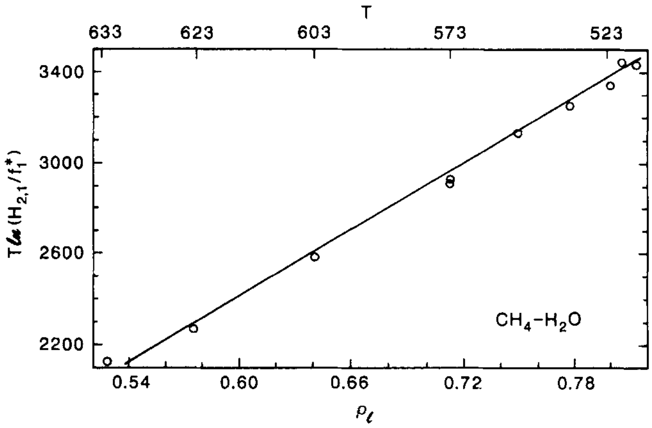

Figure 4. Henry's constant for CH_4 in water.

Same convention as in Figure 2

Critique

That the behavior of Henry's constant is more fruitfully linked to the solvent density than to its temperature, has been suggested before (Preston et al., 1971; Potter and Clynne, 1978). Our results show this to be a thermodynamic necessity near the solvent's critical point.

As discussed before, Beutier and Renon (1978) tried to determine the temperature derivative of $S_{21}^{-1} \equiv H_{2,1}/\phi_2^\infty$, which is, given the operational character of S_{21}, a more practical question to ask than determining the temperature derivative of Henry's constant $H_{2,1}$, or of $H_{2,1}/f_1^*$, as we have done. Beutier and

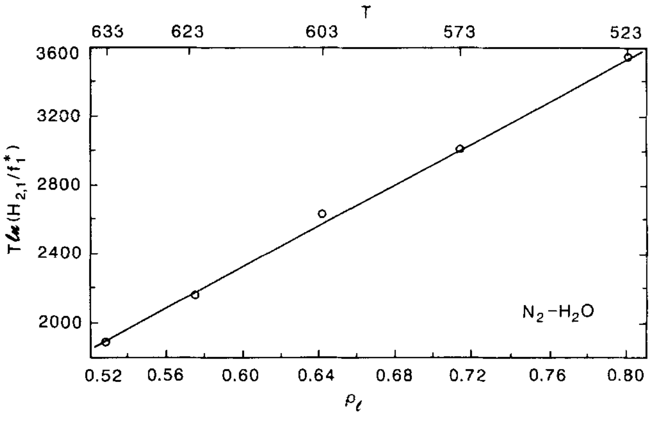

Figure 5. Henry's constant for N_2 in water.

O Data of Japas and Franck (1985); same convention as in Figure 2

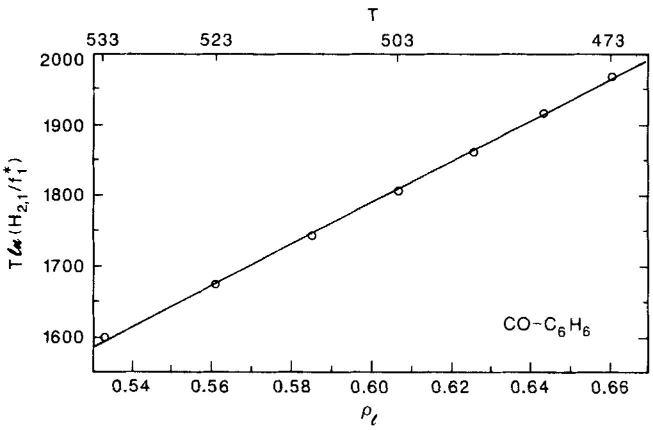

Figure 6. Henry's constant for CO in C_6H_6.
○ Data for Connolly and Kandalic (1984); same convention as in Figure 2

Renon, however, did not pursue the limiting behavior of $d\phi_2^\infty/dT$, as we did for df_1^*/dT. Although the latter derivative remains finite, the former diverges, so that our approach determines $dH_{2,1}/dT$, which they did not set out to do. Schotte (1985) criticized the derivation of Beutier and Renon because derivatives of γ_2, γ_1, ϕ_1, and the Poynting corrections with respect to temperature were neglected. Although this criticism in principle was justified, both the present work and that of Levelt Sengers (1989) demonstrate that none of these derivatives contributes to the divergence of the slope of $H_{2,1}$.

The one serious difficulty with the proof of Beutier and Renon is that they used the two-phase critical isobar as the path of approach to the critical point. Along this path, x and y are finite, so it is not possible to define the infinite-dilution solubility or take the Henry's law limit at any point except the critical point of the solvent. It is, however, necessary to take the limit $x \rightarrow 0$ before any manipulation of Henry's constant can be undertaken.

Schotte's derivation, on the other hand, appears to take the critical line as the path of approach (his Eq. 16 is only valid along the critical line). For the same reason as before, x and y being finite, this path plays no role in the problem at hand except insofar as the initial slopes of the critical line determine the amplitude of the divergence, through our Eq. 15. Schotte, in his Eq. 32, relates the limiting value of $d \ln H_{2,1}/dT$ at the solvent's critical point to the limiting value of $d \ln x_2/dT|_{CRL}$ at this point, and finds the sign of $d \ln H_{2,1}/dT$ by observing that $dx_2/dT|_{CRL}$ is negative for volatile solutes. This, however, is incorrect because $dx_2/dT|_{CRL}$ can have either sign. For instance, it is negative for nitrogen in water, and positive for helium in water (Franck, 1987). The sign of the divergence of the slope of Henry's constant, according to our result, Eq. 25, is the opposite of that of $(\partial p/\partial x)^c_{VT}$. The sign of the latter quantity is positive for both systems, even though the critical line goes through a temperature minimum in the system N_2-H_2O, but not in He-H_2O.

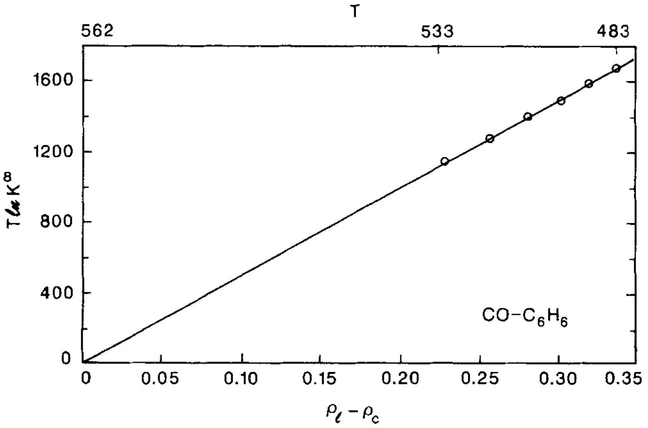

Figure 7. Infinite-dilution K factor for CO in C_6H_6: $T \ln K^\infty$ in K as a function of $\rho_l - \rho_c$ of pure benzene in kg · dm^{-3}.
Data as in Figure 5; this function must pass through the origin

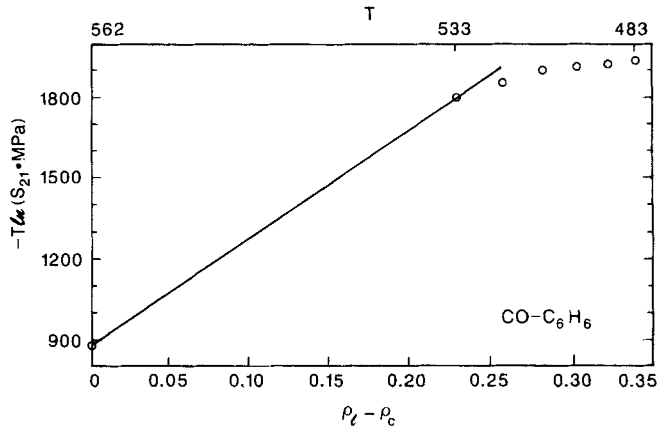

Figure 8. Infinite-dilution solubility for CO in C_6H_6: $-T \ln (S_{21} \cdot \text{MPa})$ in K as a function of $\rho_l - \rho_c$ of pure benzene in kg · dm^{-3}.
Intercept must equal $-T \ln (P_c^{-1} \cdot \text{MPa})$
The asymptotic range for the solubility parameter defined by Beutier and Renon (1978) is obviously much smaller than for the infinite-dilution properties in Figures 6 and 7

Conclusions

In determining the character of critical anomalies in dilute mixtures, it is essential to specify the path of approach, since it is well known that not only the amplitudes and exponents of critical divergences, but also the infinite-dilution values of finite properties depend on the path of approach (Wheeler, 1972; Chang et al., 1984).

The key to obtaining the correct temperature derivative for the coefficient $H_{2,1}$ in Henry's law and the limiting solubility S_{21}, is the realization that the system is in two phases and that the limit $x \rightarrow 0$ is to be taken first, so that the path to the solvent's critical point is the pure-fluid coexistence curve. There are only three properties to consider, one being the $x = 0$ limit of the ratio y/x, the others the pair $A_x^{r\infty}$, $A_y^{r\infty}$, infinite-dilution limits of the

Table 1. Values of A^c_{Vx}

	$-A^c_{Vx} \times 10^{-3}$ MPa	
System	From Critical Line	From Henry's Constant
H_2-H_2O	0.16	0.16
N_2-H_2O	0.22	0.20
CH_4-H_2O	0.15	0.17

composition derivatives of the residual Helmholtz free energy in liquid and vapor.

$A_x^{r\infty}$ and $A_y^{r\infty}$ both vary as the density difference with the solvent's critical density, and therefore have, asymptotically, diverging temperature derivatives of the same amplitude, but of opposite signs. The former determines the behavior of $d \ln H_{2,1}/f_1^*)/dT$. The quantity $\ln y/x$ behave as $A_x^{r\infty} - A_y^{r\infty}$ and therefore its temperature derivative diverges with the same exponent but with twice the amplitude as each of the free energy derivatives; $\ln (y/x)$ determines the behavior of dS_{21}/dT and of the K factor.

Finally, we should clarify an apparent paradox alluded to in the beginning of the paper. The relations (Wilhelm, 1982)

$$(\partial \ln H_{2,2}^I/\partial T)_p = (H_2^0 - \overline{H}_2^\infty)/RT^2$$
$$(\partial \ln H_{2,2}^I/\partial p)_T = \overline{V}_2^\infty/RT \tag{31}$$

coupled with the knowledge that $\overline{V}_2^\infty$, $\overline{H}_2^\infty$ diverge strongly (γ-like) at the solvent's critical point, would lead one to expect a γ-type divergence for the temperature derivative of the coefficient in Henry's law. It should be realized, however, that Eqs. 31 refer to an infinite-dilution, one-phase state, indicated in Eq. 31 by the superscript I. This $H_{2,1}^I$, equal to $\lim_{y\to 0} f_2/y$, is a function of two independent variables, such as p and T, one of which is kept constant in the differentiations in Eqs. 31. At saturation, $H_{2,1}^I$ and $H_{2,1}^{II}$ are related by

$$H_{2,1}^{II} = H_{2,1}^I \cdot \lim_{x\to 0} y/x \tag{32}$$

The two partial derivatives and the total derivative we studied are related by (Wilhelm, 1982):

$$RT^2\left(\frac{\partial \ln H_{2,1}^I}{\partial T}\right)_p = RT^2\frac{d \ln H_{2,1}^I}{dT}\bigg|_\sigma - T\frac{dp}{dT}\bigg|_\sigma\left(\frac{\partial \ln H_{2,1}^I}{\partial P}\right)_T \tag{33}$$

Our result shows that the strong divergences of the two partial derivatives cancel. A simple example will suffice to show that this is possible. For the density, ρ_1, of a one-component system we have, in analogy with Eq. 33:

$$\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p = \frac{1}{\rho}\frac{d\rho}{dT}\bigg|_\sigma - \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T\frac{dp}{dT}\bigg|_\sigma \tag{34}$$

The two partials represent, respectively, the strongly divergent expansion coefficient and compressibility. The total derivative of ρ, in view of the fact that $(\rho - \rho_c) \propto |T - T_c|^\beta$, has a $(\beta - 1)$ type divergence. The two γ-type divergences of ρ cancel exactly.

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Notation

A = Helmholtz free energy $A(V, x, T)$
A_x, A_y = composition derivatives of A
f_i = fugacity of ith component
H_1^* = enthalpy of pure first component (solvent)
$\overline{H}_i$ = partial molar enthalpy of ith component
K = partition coefficient of solute
H_i^0 = standard enthalpy of pure ith component in ideal gas state
$H_{2,1}$ = constant in Henry's law for gas (2) in solvent (1)
p = pressure
Q = composition-related function, Appendix B
R = gas constant
S = entropy
S_{21} = infinite-dilution solubility of gas (2) in solvent (1)
T = temperature
V = molar volume
$\overline{V}_i$ = partial molar volume of ith component
x = mole fraction of solute in liquid
y = mole fraction of solute in vapor

Greek letters

β = critical exponent characterizing coexistence curve
γ = critical exponent characterizing compressibility
γ_i = activity coefficient of ith component
ζ = field variable conjugate to composition, Appendix B
μ_i = chemical potential of ith component
ρ = molar density
ϕ_i = fugacity coefficient of ith component

Subscripts

c = evaluated at solvent's critical point
l = saturated liquid phase
v = saturated vapor phase
1 = first component; solvent
2 = second component; solute
σ = vapor-liquid saturation state of pure solvent

Superscripts

c = evaluated at solvent's critical point
r = residual
∞ = infinite dilution
* = pure solvent

Appendix A

In this paper we have repeatedly made unproven statements about the asymptotic behavior of thermodynamic derivatives occurring in our equations. The paper by Griffiths and Wheeler (1970) presents the principles by which the different types of critical behavior (strongly divergent, weakly divergent, nondivergent) can be predicted from the structure of the derivative in question. Two papers, by Chang et al. (1984) and Chang and Levelt Sengers (1986), specialize to dilute mixtures.

The principal distinction to be made is between density and field variables, the latter, such as p, T, μ_i, f_i being equal in coexisting phases, and the former, such as H, S, V, x, generally unequal. The rules of Griffiths and Wheeler apply to partial derivatives of densities with respect to field while c more variables are kept constant; here c is the number of components. If all these variables kept constant are themselves fields, then, both classically and nonclassically, the resulting derivative diverges strongly at the critical point (line, space). If only one of them is a density, a weak divergence results while, classically, the derivative does not diverge. If more than one density is kept constant, the derivative does not diverge. These rules apply when the critical line (space) and coexistence surface (space) in field space have no special orientation with respect to the physical field variables.

The single most important property in the present paper is $(\partial p/\partial x)_{VT}$. For a classical residual Helmholtz free energy $A(VTx)$, which is analytic in all its variables, it is clear that $(\partial p/\partial x)_{VT}$ is analytic anywhere in the one-phase region, including the critical line. Nonclassically, however, $(\partial x/\partial p)_{VT}$ is a weakly diverging property since it is the derivative of a density, x, with respect to a field, p, with one density, V, kept constant (Griffiths and Wheeler, 1970), so that $(\partial p/\partial x)_{VT}$ goes to zero weakly on the critical line. The limit of $(\partial p/\partial x)_{VT}$ at $x = 0$, however, is finite and well behaved (Chang and Levelt Sengers, 1986) even at the critical point, where it is given by Eq. 15.

The other derivative we have encounterd is $A_x^{r\infty}$ and its volume and temperature derivatives, Eqs. 20, 22. Classically, in view of the analyticity of $A^r(VT_x)$, it is obvious that all these derivatives are finite. In general, the volume derivative of A_x, being equal to $-(\partial p/\partial x)_{VT}$, Eq. 22, will be finite and nonzero if lim $x \longrightarrow 0$ is taken first. This derivative goes weakly to zero at the critical line, but this is a path we have not taken. The temperature derivative of A_x^r, according to Eq. 21, equals $-(\partial S^r/\partial x)_{VT}$, which is the derivative of a density S^r with respect to a density x. By writing

$$\left(\frac{\partial S^r}{\partial x}\right)_{VT} = \frac{(\partial S^r/\partial p)_{VT}}{(\partial x/\partial p)_{VT}}$$

and by using again the principle of Griffiths and Wheeler that derivatives of densities such as S and x, with respect to fields such as P, are weakly divergent if one density (V) is kept constant in the differentiation, we conclude that $(\partial S^r/\partial x)_{VT}$, the ratio of two weakly divergent quantities, must remain finite everywhere including the critical line.

Appendix B

The nonclassical asymptotic behavior of Henry's constant is obtained from the exact expression

$$\ln(H_{2,1}/f_1^*) = \lim_{y\to 0} A_y^r/RT + \lim_{y\to 0} \ln(y/x) \qquad \text{(B1)}$$

with A^r the residual molar Helmholtz free energy, f_1^* the fugacity of the pure solvent, and y referring to the composition of the vapor, x that of the liquid.

We use the Leung-Griffiths model (1973) in the version of Chang and coworkers (1983, 1986) to determine the asymptotic behavior and temperature dependence of $\ln(H_{2,1}/f_1^*)$. In this model, the dependent variable is p/RT and the independent variables are μ_1/RT, μ_2/RT, and $1/RT$. As a field variable that is conjugate to an appropriately defined composition variable, one defines

$$\zeta = C_2 \exp(\mu_2/RT) \Big/ \{C_1 \exp(\mu_1/RT) + C_2 \exp(\mu_2/RT)\} \qquad \text{(B2)}$$

It is readily checked that as x varies from 0 to 1, so does ζ; however, ζ is equal in coexisting phases whereas x is not.

The mole fraction x is related to ζ by

$$x = \zeta + \zeta(1 - \zeta)Q/\rho \qquad \text{(B3)}$$

where ρ is the molar density of the mixture and Q is given by an expression of the form

$$Q = Q_1 - \rho Q_2 \qquad \text{(B4)}$$

Q_1, Q_2 are complex in structure. For the present application, all we need to know is that they are smooth functions of ζ, equal in coexisting phases and generally well-behaved functions of temperature. (The temperature derivative of Q_1 has a weak critical anomaly, which is of no concern because, for the problem at hand, the temperature derivative of ρ dominates the behavior of Q). Since

$$(\partial A/\partial x)_{VT} = \mu_2 - \mu_1$$

it is easy to derive from Eq. B2 that

$$\frac{A_y^r}{RT} = \ln\frac{\zeta}{y} - \ln\frac{(1 - \zeta)}{(1 - y)} \qquad \text{(B5)}$$

so that the first term on the righthand side of Eq. B1, with y from Eq. B3, assumes the value

$$A_y^{r\infty} = \lim_{y\to 0} A_y^r = -RT \ln[1 + Q_v/\rho_v] \qquad \text{(B6)}$$

where the subscript v refers to the vapor phase (of the pure solvent). Similarly, we have, for the second term in Eq. B1:

$$\lim_{y\to 0} \ln(y/x) = \frac{1 + Q_v/\rho_v}{1 + Q_l/\rho_l} \qquad \text{(B7)}$$

so that

$$\ln(H_{2,1}/f_1^*) = -\ln(1 + Q_l/\rho_l) \qquad \text{(B8)}$$

We have already noted, in Eq. B4, that $Q_l = Q_1 - \rho_l Q_2$, with Q_1, Q_2 having at most weakly diverging temperature derivatives at the coexistence curve. The direct density dependence of Eq. B8 thus determines the dominant asymptotic temperature dependence of $\ln(H_{2,1}/f_1^*)$. Thus

$$\ln(H_{2,1}/f_1^*) = -\ln(1 + Q_1/\rho_l - Q_2) \qquad \text{(B9)}$$

and, with $\rho_l = \rho_c + \Delta\rho_l$, we have, for small $\Delta\rho_l$:

$$\frac{d\ln(H_{2,1}/f_1^*)}{dT} = \frac{Q_1^c/\rho_c^2}{(1 + Q^c/\rho_c)}\frac{d\Delta\rho_l}{dT} \qquad \text{(B10)}$$

Since $\Delta\rho_l \sim |\Delta T|^\beta$, the temperature derivative in Eq. B10 has a critical exponent of $\beta - 1$. In Eq. 30 of Chang and Levelt Sengers (1986) it is shown that

$$\left(\frac{\partial p}{\partial x}\right)_{VT}^c = -A_{Vx}^c = \frac{RT_c Q_1^c}{(1 + Q^c/\rho^c)} \qquad \text{(B11)}$$

Therefore

$$RT\frac{d\ln(H_{2,1}/f_1^*)}{dT} \simeq -A_{Vx}^c \frac{d\Delta\rho_l/\rho_c^2}{dT} \qquad \text{(B12)}$$

For a volatile solute, A_{Vx}^c is negative; the sign of the derivative of the liquid density is likewise negative. Thus, we retrieve the same asymptotic expression, with a negative value, for the temperature dependence of $\ln(H_{2,1}/f_1^*)$ in both the classical case, Eq. 14, and the nonclassical case, Eq. B12, with a critical exponent of $\beta - 1$.

Appendix C

Experimental isothermal solubility data, ideally values of x and y over a range of pressures exceeding p_σ, require considerable manipulation in order to yield Henry's constant or solubility values such as those we display in Table 1 and Figures 1–6. Even more calculation is required if the composition of only one of the phases (usually the liquid) is known. Here we summarize the principles involved. For details, we refer to the papers by Crovetto and coworkers (1982, 1988). These authors obtained Henry's constant by equating the chemical potential of the solute in liquid and vapor phase:

$$RT \ln (H_{2,1} x \gamma_2) + \int \bar{V}_2 \, dp = RT \ln (p y \phi_2) \qquad \text{(C1)}$$

A (generally small) Poynting correction was made by estimating $\bar{V}_2$ from a perturbed-hard-sphere equation of state for the liquid. The activity coefficient γ_2 was also calculated this way. They calculated the fugacity coefficient ϕ_2 of the solute in the vapor from the Peng-Robinson equation. In the cases where the composition y was not measured, it was calculated iteratively by equating the chemical potentials of the solvent in the liquid and vapor phase.

$$RT \ln f_1 + \int \bar{V}_1 \, dp = RT \ln \{p(1 - y)\phi_1\} \qquad \text{(C2)}$$

with

$$f_1 = (1 - x)\gamma_1 p_1^* \phi_1^* \qquad \text{(C3)}$$

The asterisks refer to pure-solvent properties, which were taken from the tables by Haar et al. (1984). $\bar{V}_1$ and ϕ_1 were calculated from the Peng-Robinson equation of state, with an initial guess for y. Equation C2 was iterated for the experimental value of x until the the value of y converged. The above procedures are fraught with peril if applied near the solvent's critical point. The following tests of validity were made by the authors.

1. It was checked that the Peng-Robinson parameters used resulted in accurate values of ϕ^* for pure water.

2. In cases where x, y data from other sources were available (up to 200°C for water) the procedure was found to be as accurate as the y data, $\sim 1\%$.

3. In the case of N_2-H_2O, some values of y were measured up to 350°C. Again, the procedure was found accurate on the level of accuracy of the y data, $\sim 3\%$. The procedure was never applied any closer than 24 K from the steam critical point.

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