Correlation of Aqueous Henry's Constants from 0°C to the Critical Point

Recent theoretical results (Japas and Levelt Sengers, 1989) for the temperature dependence of Henry's constant near the solvent's critical point are used to obtain a linear expression which, for aqueous solutions of nonpolar gases, fits experimental Henry's constant data at temperatures from water's critical point down to roughly the normal boiling point. A small correction with only one additional adjustable parameter extends the correlation to 0°C. The final result is a three-parameter correlation, covering the entire range of temperatures, which fits the available data as well as or better than existing four-parameter empirical expressions and better than a recently proposed three-parameter expression. Since the correct near-critical behavior is built in, the new correlation should be especially useful for estimating Henry's constants in systems where little or no data exist at high temperatures. Fitted parameters are given for ten nonpolar gases in H_2O and six nonpolar gases in D_2O.

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Introduction

At low and moderate pressures, description of the solubility of gases in liquids is usually based upon Henry's law (see, for example, Prausnitz et al., 1986). The variation of Henry's constant k_H with temperature is not simple. After an initial increase with temperature, k_H goes through a maximum (different for each solute in a given solvent) and declines at higher temperatures. In the limit as the critical point of the solvent is approached, Henry's constant remains finite but its derivative with respect to temperature diverges (Beutier and Renon, 1978; Japas and Levelt Sengers, 1989).

While it is possible to obtain Henry's constants at different temperatures from thermodynamic perturbation theory (Fernandez Prini et al., 1985) or scaled-particle theory (Wilhelm, 1973; Schulze and Prausnitz, 1981), the results are very sensitive to the solute-solvent collision diameter which must be made temperature-dependent. In general, theoretical models at the molecular level have not been successful in describing the behavior of k_H over the wide range of temperature with which we are concerned here.

Experimental Henry's constant data are typically correlated using polynomials in reciprocal temperature or other largely empirical equations; four adjustable parameters are usually required if a wide range of temperature is covered. Extrapolation of these equations outside the range of data fitted is unreliable, especially at high temperatures where they do not exhibit the correct limiting behavior as the solvent critical temperature is approached.

Recently, Japas and Levelt Sengers (1989) examined the behavior of Henry's constant in the neighborhood of the solvent critical point. They showed that the product $T \ln(k_H/f_1^s)$, where T is the absolute temperature and f_1^s is the fugacity of the pure solvent at saturation, varies linearly with the density of the solvent. While this is an asymptotic result, we will show that the limiting behavior can be used as the basis for a simple three-parameter correlation for Henry's constants over the entire range of temperature. For the aqueous solutions of nonpolar gases examined in this work, the new three-parameter expression provides a description of Henry's constant data over a wide range of temperature which is as good as and often better than the existing four-parameter correlations. Furthermore, since the parameters are thermodynamically meaningful and since the correct limiting behavior is obtained at high temperatures, the new expression is better suited for extrapolation and interpolation in systems where only limited high-temperature data exist.

Theory

The Henry's constant for a solute (2) in a solvent (1) is defined by

$$k_H = \lim_{x_2 \to 0} (f_2/x_2) \tag{1}$$

where f_2 is the fugacity and x_2 the liquid-phase mole fraction of component 2. While it is possible to apply this definition in the one-phase region, we will for the purposes of this paper restrict our discussion to values of k_H along the saturation curve of the solvent; these are the values of most use in phase-equilibrium calculations. For a given solute in a given solvent, k_H is then a function of only one variable; it is customary to describe it as a function of temperature.

Japas and Levelt Sengers (1989) showed that, in the neighborhood of the critical point of the solvent, the following linear relationship is dictated by thermodynamics:

$$T \ln (k_H/f_1^s) = A + B(\rho_1^s - \rho_{c,1}) \tag{2}$$

where ρ_1^s is the saturated-liquid density and $\rho_{c,1}$ the critical density of the solvent, component 1. A and B are constants and can be fitted to data, but they are also thermodynamically meaningful. Examination of Eq. 2 at the solvent critical point shows that A may be written as

$$A = T_{c,1} \ln (\phi_{2,c1}^{\infty} P_{c,1}/f_{c,1}) \tag{3}$$

where $T_{c,1}$, $P_{c,1}$, and $f_{c,1}$ are the temperature, pressure and fugacity of component 1 at its critical point. $\phi_{2,c1}^{\infty}$ is the fugacity coefficient of component 2 evaluated at infinite dilution at the solvent critical point. $\phi_{2,c1}^{\infty}$ is the only solute-dependent variable affecting k_H at the critical point; this was pointed out by Beutier and Renon (1978). B is related to the composition dependence of the pressure at the critical point:

$$B(R\rho_{c,1}^2) = (\partial P/\partial x)_{V,T}^c \tag{4}$$

where R is the molar gas constant. This derivative can be related to the limiting slope of the solvent vapor pressure curve and to the initial slope of the critical line (Krichevskii, 1967; Chang et al., 1984):

$$(\partial P/\partial x)_{V,T}^c = dP/dx\,|_{CRL}^c - [dP/dT|_\sigma^c][dT/dx\,|_{CRL}^c] \tag{5}$$

where subscript σ indicates a derivative evaluated along the vapor pressure curve and subscript CRL indicates that the path is along the critical line of the binary mixture.

For the aqueous systems considered here, neither critical-line slopes nor values of $\phi_{2,c1}^{\infty}$ are known well enough to allow *a priori* prediction of A and B. However, the relation of these parameters to well-defined thermodynamic quantities suggests that Eq. 2 could provide a basis for a better correlation than those in which the adjustable parameters are merely empirical.

New Correlation

Development of a correlation required a consistent set of Henry's constant data. Details of data selection, evaluation and fitting are given in the Appendix. We focused on Henry's constants of nonpolar gases in water because there is a relatively large amount of data available for these systems and also because water is the solvent of the most interest in practical applications. For water, the pure-solvent densities and fugacities required in the correlation may be readily obtained from steam tables (Haar et al., 1984) which are available in computerized form. The value 322 kg/m³ (17.87 mol/L) was used for $\rho_{c,1}$ (Kestin et al., 1984a).

Equation 2 is, as we have mentioned, only an asymptotic relation. However, we found that the linear relationship suggested by Eq. 2 holds over a very large range of temperature. Figure 1, for oxygen in water, shows $T \ln (k_H/f_1^s)$ plotted vs. ρ_1^s; the temperature scale is shown at the top of the figure. Figure 2 shows a similar plot for nitrogen (It should be noted that the maxima in these plots do not correspond to maximum values of k_H.) As can be seen in these figures, the simple linear relationship is consistent with experimental data down to roughly the normal boiling point. This was the case for all ten nonpolar gases examined in this work.

Although Eq. 2 provides a simple two-parameter correlation for Henry's constants at temperatures above 373 K, we felt that it would be even more useful to develop a correlation covering the entire range of temperature. Examination of fits such as those shown in Figures 1 and 2 indicated that the deviation from the linear relationship was approximately an exponential decay in ln k_H with temperature. Consequently, we added an empirical exponential term to Eq. 2, producing the following relation:

$$T \ln (k_H/f_1^s) = A + B(\rho_1^s - \rho_{c,1}) + C\,T\rho_1^s \exp[(273.15 - T)/\tau] \tag{6}$$

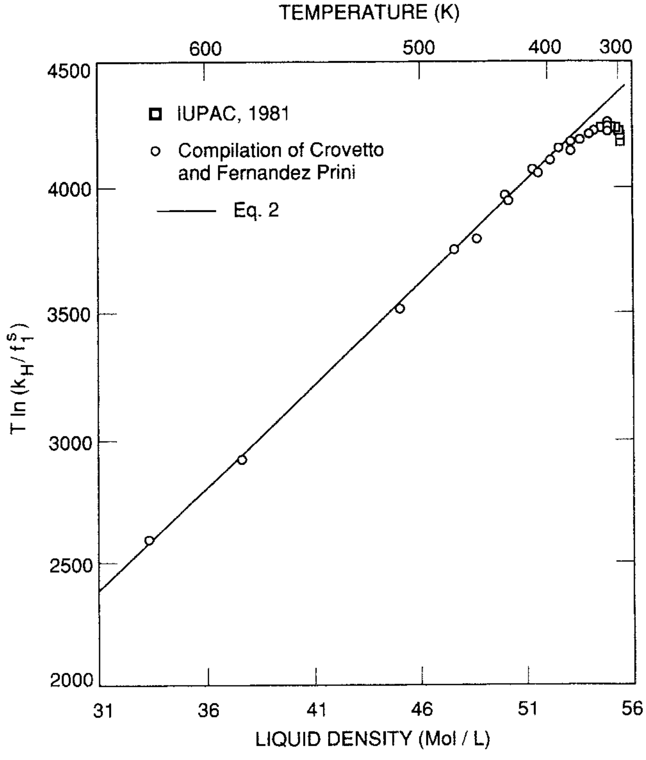

Figure 1. Linear relationship of $T \ln (k_H/f_1^s)$ vs. ρ_1^s for O_2 in H_2O.

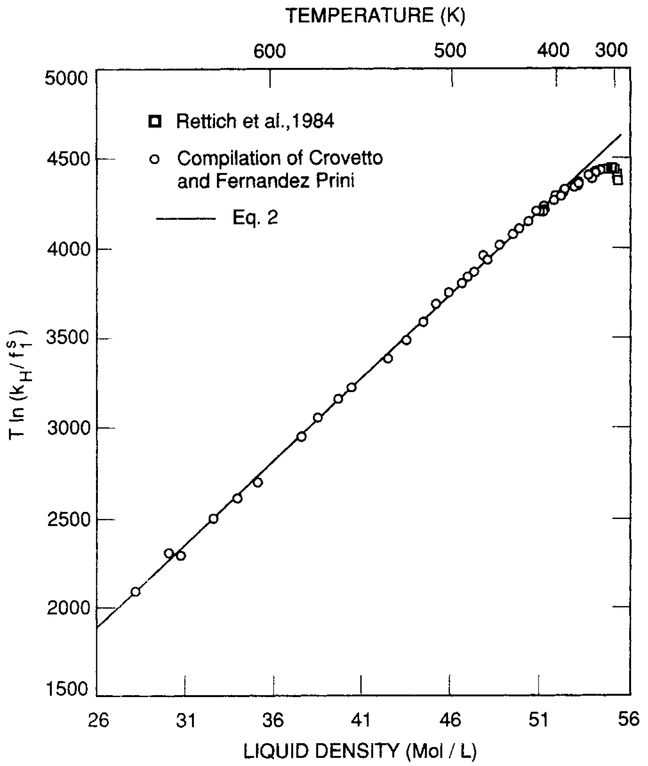

Figure 2. Linear relationship of $T \ln (k_H/f_1^s)$ vs. ρ_1^s for N_2 in H_2O.

where C and τ are adjustable parameters. C represents the amplitude and τ the decay constant of the exponential departure from the linear function. It was found that τ was nearly the same for all the systems examined. τ was therefore set to a universal value of 50 K; fixing this value did not significantly worsen any of the fits. Equation 6 is then a three-parameter correlation for k_H covering all temperatures from 0°C to the critical point.

Results

Equation 6 (with τ = 50 K in all cases) was fitted to experimental Henry's constants for ten nonpolar gases in water. Table 1 lists the optimum parameters along with other information about the fits. Figures 3 and 4 show ln k_H as a function of temperature for hydrogen and methane; these are (in addition to oxygen and nitrogen) the systems where data exist at the highest temperatures. Figure 5 shows the same plot for krypton; in this case there are not as many data and the high-temperature portion of the curve represents an extrapolation. In these and all the other cases, the new three-parameter expression fits the data to within the experimental scatter except perhaps at the lowest temperatures where the data are very precise.

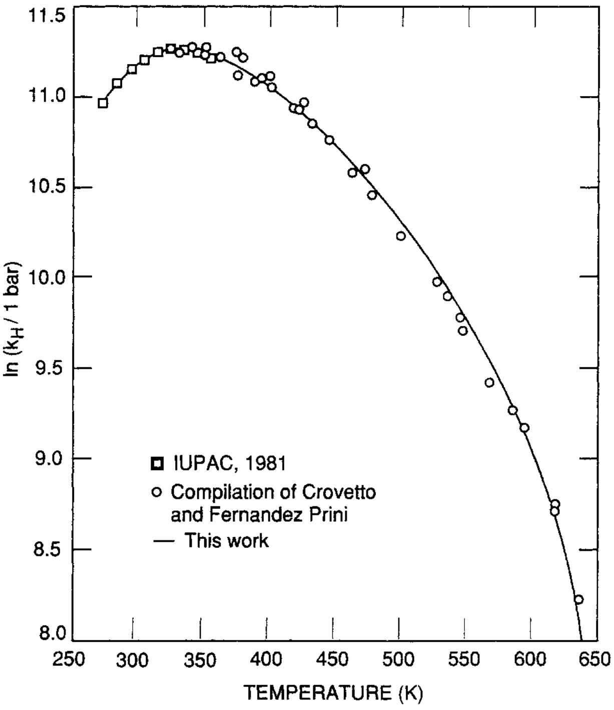

Figure 3. Henry's constants for H_2 in H_2O.

Several empirical and semiempirical correlating equations exist against which this work may be compared. The simplest is the commonly used polynomial expansion in inverse temperatures:

$$\ln k_H = A_0 + A_1/T + A_2/T^2 + A_3/T^3 \qquad (7)$$

The three-term version of this polynomial was, for most systems, found to be completely inadequate for covering a wide temperature range. The four-term polynomial provides a reasonable fit in many cases and results from Eq. 7 will subsequently be designated by the label POLY4.

In order to obtain better results at high temperature for their nitrogen and hydrogen data, Alvarez et al. (1988) removed the

Table 1. Parameters for Correlation of Aqueous Henry's Constants with Eq. 6

Solute	A K	B K · L/mol	C L/mol	# Pts	Max. T K
H_2	1,169.7	84.72	0.00203	42	636.13
He	917.9	95.88	0.00602	15	553.15
Ne	1,662.1	76.13	0.00086	13	543.4
Ar	1,513.5	74.71	−0.01210	15	568.4
Kr	1,516.5	71.10	−0.01640	12	525.6
Xe	880.3	86.08	−0.02513	20	574.82
N_2	1,136.5	92.68	−0.01848	51	636.5
O_2	1,319.6	81.40	−0.01483	27	616.48
CH_4	1,025.8	88.96	−0.01682	38	633.15
C_2H_6	651.5	101.31	−0.03356	20	473.5

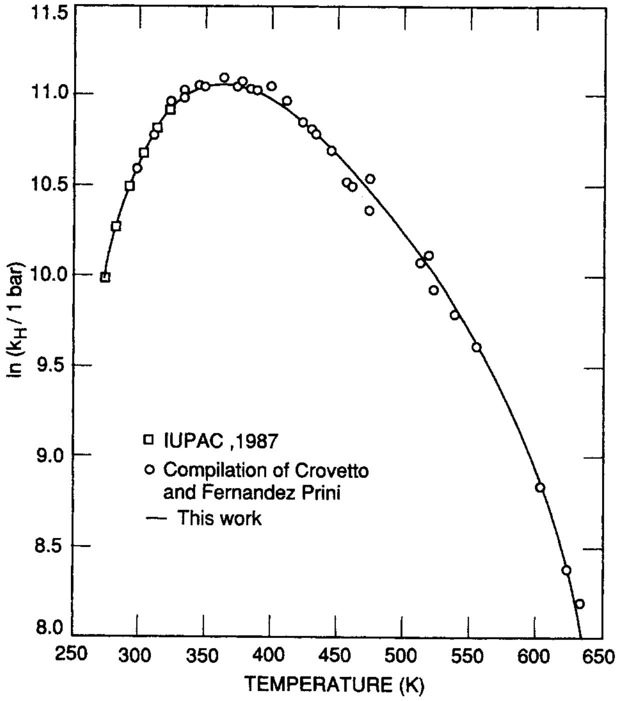

Figure 4. Henry's constants for CH_4 in H_2O.

final term from Eq. 7 and added a term whose derivative diverges at the critical point:

$$\ln k_H = A_0 + A_1/T + A_2/T^2 + B_0[(T_{c,1} - T)/T] \ln [(T_{c,1} - T)/T_{c,1}] \quad (8)$$

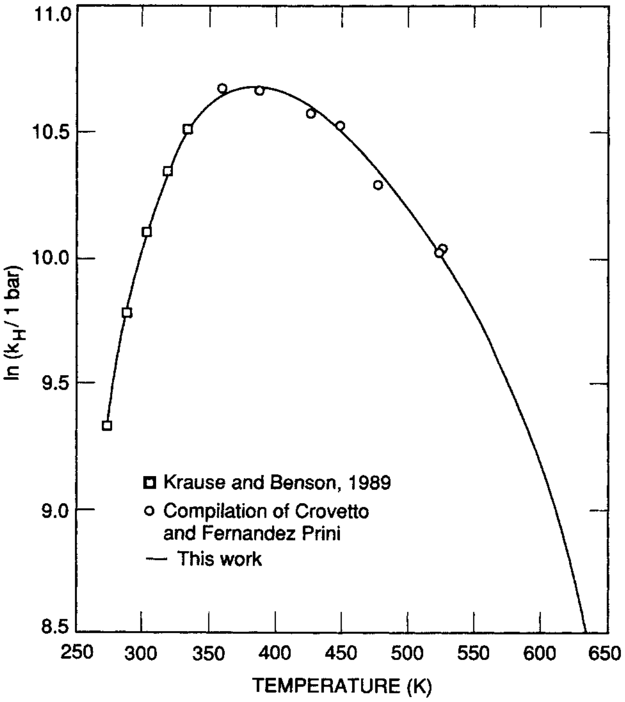

Figure 5. Henry's constants for Kr in H_2O.

Results from Eq. 8 will be designated by POLY3+B. We have followed Alvarez et al. in using $T_{c,1}$ = 647.3 K for water in our fits using Eq. 8; using the currently accepted value of 647.14 K makes no noticeable difference.

Very recently, Fernandez Prini and Crovetto (1989) have used Eq. 8 with B_0 set at a fixed value of -1 and the fourth polynomial term restored:

$$\ln k_H = A_0 + A_1/T + A_2/T^2 + A_3/T^3 - [(T_{c,1} - T)/T] \ln [(T_{c,1} - T)/T_{c,1}] \quad (9)$$

We will refer to this as POLY4+.

We also examined the Clarke-Glew (1966) expression:

$$\ln k_H = A_0 + A_1/T + A_2 \ln T + A_3 T \quad (10)$$

The three-term version (without the term linear in T) is also known as the Valentiner (1927) equation; it was clearly inadequate in most cases. Results from the four-parameter Eq. 10 are designated as CG4.

Finally, we examined the three-parameter expression recently presented by Krause and Benson (1989):

$$T^{*2} \ln k_H = T^{*2} A_0 + A_1(1 - T^*)^{1/3} + A_2(1 - T^*)^{2/3} \quad (11)$$

where $T^* = T/T_{c,1}$. Results from Eq. 11 are labeled as KB3.

Table 2 lists the standard deviations for each gas for our correlation and for the others described above. For systems with very limited high-temperature data (He, Ne, Ar, Kr, C_2H_6), the four-parameter empirical correlations are also able to fit the relatively small number of points to within experimental uncertainty; in some cases the extra adjustable parameter produces a smaller standard deviation than our method. However, comparisons for the systems with much more extensive data at high temperatures (H_2, N_2, CH_4) make it clear that POLY4, POLY4+, and CG4 are inferior in their ability to fit high-temperature data. The three-parameter KB3 correlation does well for most of the systems, but its inadequacy at high temperatures is also evident in the hydrogen, nitrogen and methane systems. The only correlation other than Eq. 6 which is consistently able to fit the data within the experimental scatter is POLY3+B; this four-parameter expression produces standard deviations which are for the most part slightly smaller than those for the new three-parameter correlation. (See the next section, however, for a problem with POLY3+B.)

Critical Behavior

At this point it is appropriate to comment on the critical behavior of the correlations examined. Theory dictates that the divergence of $d(\ln k_H)/dT$ as $T \rightarrow T_{c,1}$ along the saturation curve is characterized by the exponent β-1 (Japas and Levelt Sengers, 1989), where the critical exponent β has a universal value of 0.326 ± 0.002 (Sengers and Levelt Sengers, 1986). This is a consequence of the linear dependence of ln k_H on density (Eq. 2) and the critical scaling relationship:

$$|\rho_1^s - \rho_{c,1}| \sim |T - T_{c,1}|^\beta \quad (12)$$

Equations 8 and 9 yield a logarithmic divergence, corresponding to an exponent of zero. Equation 11 yields a divergence with

Table 2. Standard Deviations in ln $(k_H/1 \text{ bar})$ for Eq. 6 and Other Correlations

Solute	Eq. 6	POLY4	POLY3+B	POLY4+	CG4	KB3
H_2	0.0484	0.0684	0.0361	0.0582	0.0496	0.0772
He	0.0311	0.0407	0.0310	0.0378	0.0369	0.0254
Ne	0.0261	0.0153	0.0169	0.0162	0.0151	0.0202
Ar	0.0361	0.0418	0.0391	0.0400	0.0430	0.0399
Kr	0.0276	0.0211	0.0210	0.0218	0.0207	0.0373
Xe	0.0813	0.0907	0.0843	0.0886	0.0894	0.0791
N_2	0.0367	0.0958	0.0360	0.0839	0.0680	0.0960
O_2	0.0418	0.0468	0.0384	0.0429	0.0423	0.0583
CH_4	0.0473	0.0796	0.0455	0.0697	0.0652	0.0988
C_2H_6	0.0481	0.0244	0.0222	0.0241	0.0231	0.0301

exponent $-2/3$; this is very close to the correct exponent $\beta - 1$. We would therefore expect the KB3 correlation to perform better at near-critical temperatures than the expressions with a logarithmic divergence or with no divergence at all. Even though the exponent characterizing the divergence of Eq. 11 is for all practical purposes correct, we note that the limiting law of Eq. 2 is not completely satisfied because the temperature dependence is different and the pure-solvent fugacity is not factored in.

It is also worthwhile to consider the sign of the divergence; for volatile solutes $d(\ln k_H)/dT \longrightarrow -\infty$ as the critical point is approached. For the parameters to be physically meaningful, we must therefore have $B > 0$ in Eq. 6, $B_0 < 0$ in Eq. 8, and $A_1 > 0$ in Eq. 11. The only case where this condition was violated was for krypton with Eq. 8 (POLY3+B); it was this problem with POLY3+B which led Fernandez Prini and Crovetto (1989) to propose and use POLY4+.

Results for Gases in Heavy Water

The new correlation was also used to fit the more limited data available for nonpolar gases in heavy water (D_2O). Details concerning the data and the fits are again given in the Appendix. Equation 6 was used with one modification: 273.15 was replaced by 276.97 K, the triple-point temperature of D_2O. τ was once again set at 50 K for all systems. Pure-solvent densities and fugacities were obtained from an accurate equation of state for heavy water (Hill et al., 1982). A value of 356 kg/m^3 (17.78 mol/L) was used for $\rho_{c,1}$ (Kestin et al., 1984b). Table 3 shows the results for six gases in D_2O. As was the case with H_2O, the new correlation successfully fits the available data over the entire range of temperature.

Discussion

Our new approach is in large part a matter of choosing the right coordinates on which to plot the experimental data. Once $T \ln(k_H/f_1^s)$ is graphed vs. ρ_1^s (as suggested by Eq. 2 and illustrated in Figures 1 and 2), it becomes relatively simple to correlate the data. Jonah (1983) was able to obtain straight lines over a fairly wide range of temperature for gases in organic solvents by plotting $\ln(k_H/f_1^s)$ vs. $1/T$; this implies that $T \ln(k_H/f_1^s)$ is linear in T. We can interpret this as a consequence of the fact that, over modest ranges of temperature far from the critical point, it is often not a bad approximation to say that saturated-liquid densities are linear in temperature. Over the wide range of temperature considered in this study, however, plots on Jonah's coordinates show substantial curvature. This is inevitable at high temperatures because the correct limiting law is not obeyed.

The new approach should be very useful for critical examination and smoothing of data. Aberrant data points are much easier to spot when they can be compared to a straight line. While empirical four-parameter correlations may be able to fit a given set of data as well as our three-parameter correlation, the thermodynamically correct form adopted in this work should inspire more confidence in values obtained from the smoothing equation, especially when only a few high-temperature points are available to be fitted.

Perhaps the greatest advantage of the method presented in this work is the ability to extrapolate data to higher temperatures. Given only data up to the region where the asymptotic behavior is well established, Eq. 6 may be extrapolated with reasonable accuracy all the way to the critical point. This is illustrated in Figure 6 for nitrogen in H_2O, where various correlating expressions were fitted only to data below 450 K. Our expression is able to predict the high-temperature data almost as well as when it is fitted to the entire data set, while extrapolations from the other expressions (with the exception of KB3) are substantially worse. Similar calculations for several gas/water systems showed that only Eq. 6 was consistently

Table 3. Parameters and Standard Deviations for Correlation of Henry's Constants in D_2O with Eq. 6

Solute	A K	B K · L/mol	C L/mol	# Pts	Max. T K	Std. Dev. in ln k_H
He	1,348.4	82.32	−0.01290	6	553.15	0.0466
Ne	1,796.2	71.40	0.00751	9	550.0	0.0427
Ar	1,345.1	79.75	−0.01055	19	583.8	0.0457
Kr	1,398.1	74.99	−0.01487	10	523.1	0.0402
Xe	538.6	96.51	−0.02390	9	574.82	0.0729
CH_4	1,083.5	87.92	−0.01376	13	517.5	0.0225

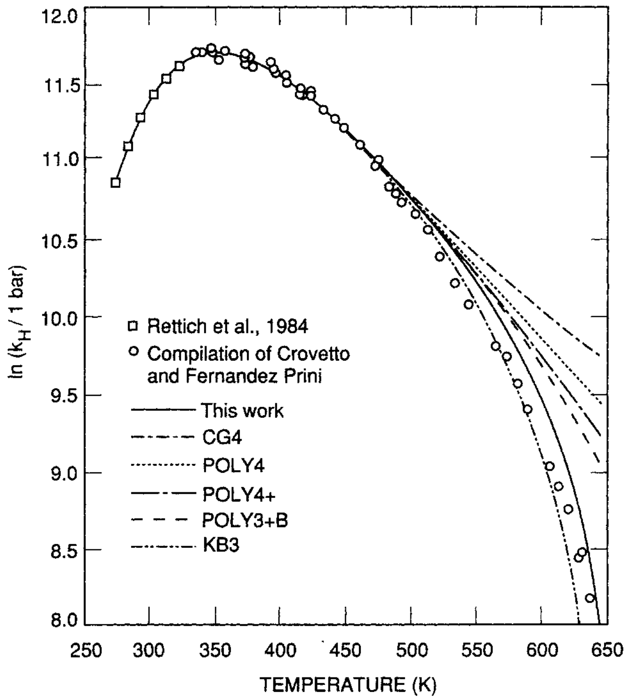

Figure 6. Henry's constants for N_2 in H_2O.
Comparison of extrapolations based on fits to data below 450 K.

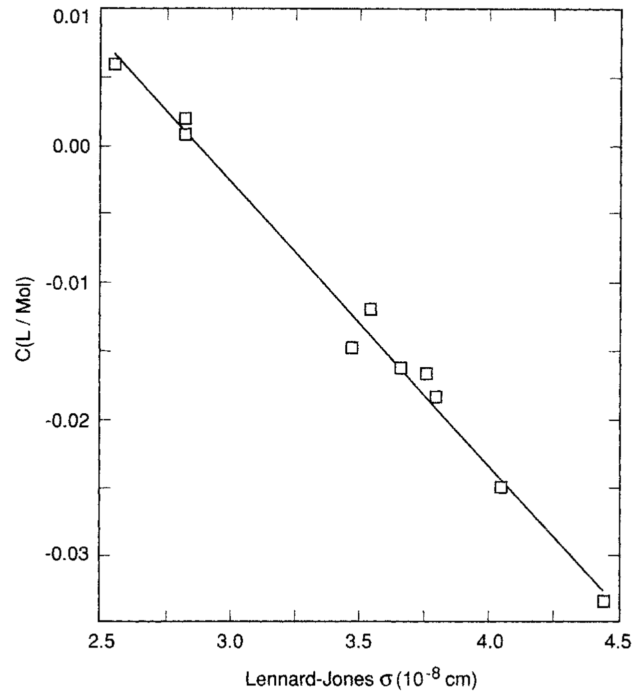

Figure 7. Correlation of parameter *C* with molecular size parameter *σ*.

reliable for such extrapolation. This is a consequence of its correct high-temperature form. KB3 (with its almost-correct critical divergence) was the best of the other expressions; the four-parameter correlations almost always produced poor extrapolations.

One additional advantage of the new correlation is the thermodynamic significance of the parameters A and B as given by Eqs. 3 and 4. While infinite-dilution fugacity coefficients at critical conditions and initial critical-line slopes are not in general known with much accuracy, Eqs. 3 and 4 can serve to check that regressed parameters are reasonable. For example, as mentioned earlier, B must be positive for volatile solutes. In earlier work from this laboratory (Japas and Levelt Sengers, 1989), some comparisons were made between values of $(\partial P/\partial x)V_{c,T}$ calculated from B via Eq. 4 and from critical lines via Eq. 5. We have since discovered that some of those values were computed incorrectly; Table 4 contains corrected values and should replace Table 1 in the earlier paper. At first sight the lack of agreement between our results and reported critical-line data might appear troubling. These critical lines, however, are not directly measured but instead are estimated from graphical manipulation of PVT data taken along paths of constant composition. The resulting uncertainties are particularly large in the region close to the critical point of water. As a result, the quantity computed in Eq. 5 is not accurately known; agreement within a factor of two is probably within the uncertainty of the calculation. It might even be argued that, since values of B seem to be well-determined, Henry's constants could be used as an aid in estimating initial critical-line slopes from experimental data.

Table 4. Values of $(\partial P/\partial x)^c_{V,T}$ (in GPa) Calculated from Critical Lines (Eq. 5) and Henry's Constants (Eq. 4)

System	From Critical Line	From k_H
H_2—H_2O	0.15	0.22
N_2—H_2O	0.18	0.25
CH_4—H_2O	0.15	0.24

We have made some preliminary attempts (using a simple van der Waals mixture model) at connecting A and B with molecular properties, but the resulting correlations are qualitative at best. This is not too surprising given the relative complexity of interactions involving water molecules. However, we find that the parameter C correlates very well with molecular size. In Figure 7, values of C are plotted vs. Lennard-Jones diameter σ (Reid et al., 1987) for the ten nonpolar gases considered in this work. The results seem to fall on a straight line, though we know of no theoretical reason to expect linearity here. Figure 7 suggests that the parameter C, which represents the low-temperature departure from the linear limiting relationship, is in some sense measuring the disruption of the water structure due to the excluded volume of the solute molecule.

Japas and Levelt Sengers (1989) derived other asymptotic relations; the one of the most practical interest involves the infinite-dilution K-factor or partition coefficient K^∞. In this case, the linear relationship found is between $T \ln K^\infty$ and the liquid density. Fernandez Prini (1989) has plotted data for a few high-temperature aqueous systems on these coordinates with good results. Working with the K-factor has the advantage that the intercept at $\rho = \rho_{c,1}$ is known since K^∞ must become unity at the solvent's critical point. For some systems, particularly those where vapor-phase compositions have also been measured at high temperatures (this is rare in gas solubility studies), it might therefore be worthwhile to correlate high-temperature data in terms of K^∞ rather than k_H.

Finally, we note that the utility of our result is not limited to solutes in H_2O and D_2O. We have performed calculations using

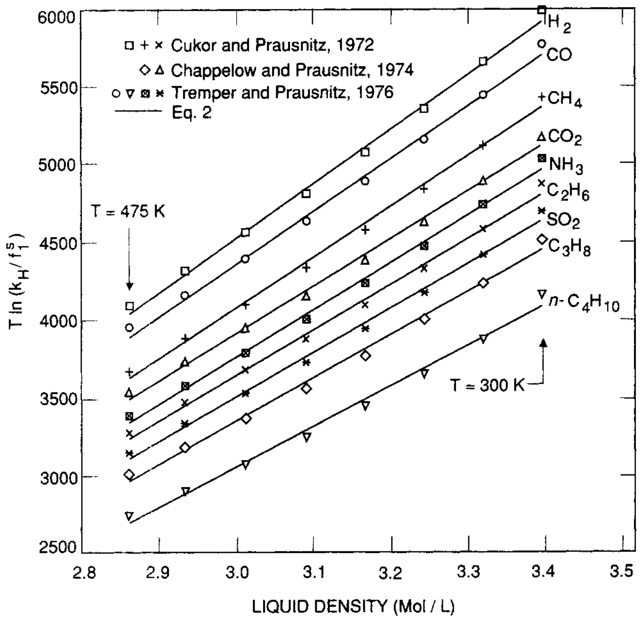

Figure 8. Linear relationship of $T \ln (k_H/f_1^s)$ vs. ρ_1^s for various solutes in n-hexadecane.
($\rho_{c,1} \approx 1.1$ mol/L)

published Henry's constants for 12 gases dissolved in n-hexadecane (Cukor and Prausnitz, 1972; Chappelow and Prausnitz, 1974; Tremper and Prausnitz, 1976). Results (on the coordinates suggested by Eq. 2) are shown in Figure 8; solutes N_2, H_2S, and HCl follow the same trend but have been omitted for clarity. Though these data do not cover a temperature range as wide as that used in our correlation of aqueous systems, it is encouraging to see that the linear relationship works well. Small deviations from linearity do occur for all the solutes. While this could well be a real effect, it might also arise from errors in estimating ρ_1^s and f_1^s for pure hexadecane or from the manner in which solubility measurements were converted to Henry's constants.

Another use for the Henry's constant correlation is the calculation of derivative properties such as partial molar volumes and partial molar heat capacities. This requires a rederivation of the asymptotic behavior for directions not along the saturation curve; differentation of the resulting expression is then straightforward. The solvent density (and in particular its derivatives with respect to pressure and temperature) is again the governing factor. The dominant role of the density has been recognized and exploited in previous correlations for partial molar volumes (Brelvi andO'Connell, 1972; Cooney and O'Connell, 1987).

Conclusions

For aqueous solutions of nonpolar gases, the theoretical limiting law for the variation of Henry's constant near the solvent critical point is obeyed over a wide temperature range extending down to roughly the normal boiling point of water. This asymptotic linear relationship can be used as the basis for a three-parameter correlation for Henry's constants from 0°C to the critical point. This correlation fits the data at least as well as (and often better than) existing three- and four-parameter correlations; because its functional form incorporates the correct near-critical behavior, it is more reliable for extrapolations to high temperatures.

It is expected that the same correlation (except perhaps for the low-temperature correction) will work for other solute/solvent systems. It can also be adapted for calculation of derivative properties such as partial molar volumes.

Acknowledgment

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Notation

A = intercept in Eqs. 2,6
A_0, A_1, A_2, A_3 = adjustable parameters in Eqs. 7-11
B = slope in Eqs. 2,6
B_0 = adjustable parameter in Eq. 8
C = amplitude of exponential correction, Eq. 6
f = fugacity
k_H = Henry's constant
K = K-factor (partition coefficient)
P = pressure
R = molar gas constant
T = absolute temperature
T^* = reduced temperature in Eq. 11
V = volume
x = liquid-phase mole fraction

Greek letters

β = critical exponent of coexistence curve
ϕ = fugacity coefficient
ρ = molar density
σ = Lennard-Jones diameter
τ = decay constant in Eq. 6, 50 K

Subscripts

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

Superscripts

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

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Appendix: *Data Sources, Evaluation and Fitting*

At high temperatures, it is not straightforward to extract Henry's constants from gas solubility measurements. This is particularly true when the vapor-phase compositions are not measured, which is usually the case. We relied on the database constructed by Fernandez Prini and Crovetto (1989; personal communications, 1989) who took all available high-temperature solubility data for ten nonpolar gases in water and in heavy water and recalculated the Henry's constants in a consistent manner. They used the Peng-Robinson equation of state to describe vapor-phase nonideality, while a separate perturbed-hard-sphere equation of state was used for the liquid phase. While this approach becomes questionable in the vicinity of the critical point, it appears to be reasonable for most, if not all, of the experimental conditions considered, and we used their values without modification.

Henry's constants at low temperatures were obtained from the *IUPAC Solubility Data Series* (1980, 1981a,b, 1982, 1987) except for the noble gases in H_2O (Krause and Benson, 1989) and nitrogen in H_2O (Rettich et al., 1984), where more recent precise measurements were available, and krypton in D_2O, where the data of Cosgrove and Walkley (1981) were used. In some cases, the reported values were not corrected for vapor-phase nonideality; we performed the correction using second virial coefficients calculated by the method of Hayden and O'Connell (1975). These corrections were always small and were usually negligible. Low-temperature points were included in the fit at ten-degree intervals beginning at 0°C (5°C for gases in D_2O) except for four gases in H_2O (helium, neon, argon, and krypton) and all gases in D_2O. In these cases, the high-temperature data were relatively sparse and fifteen-degree intervals were used to avoid distorting the fit.

Data were fitted to minimize (in the least-squares sense) the deviations between predicted and experimental values of $\ln k_H$. Minimization was performed with a modified Levenberg-Marquardt algorithm as implemented in the subroutine LMDIF. This routine is a part of the MINPACK library developed at Argonne National Laboratory.

After each data set was fitted, experimental points which deviated by more than two standard deviations were examined one at a time. If omission of a point significantly reduced the standard deviation, that point was rejected. This process was necessarily somewhat subjective, and larger deviations were tolerated at higher temperatures where more uncertainty in the data is expected. For most systems only a few points, mostly from older studies, were rejected. The neon/water and argon/water systems were exceptions; in these cases, almost all of the measurements of Potter and Clynne (1978) had to be rejected in order to obtain a smooth curve. In general, the points rejected for each system and each experimental study were approximately the same as in the work of Fernandez Prini and Crovetto (1989), who used POLY4+ as their smoothing equation. This indicates that the use of Eq. 6 did not significantly bias the selection or rejection of data points.

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