# Semiempirical Correlation for Henry's Constants over Large Temperature Ranges

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Henry's law is commonly used to describe the solubility of gases in liquids at low and moderate partial pressures. For a solute-solvent pair, Henry's constant typically increases with temperature, passes through a maximum, and then declines at higher temperatures. As the critical temperature 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).

In previous work (Harvey and Levelt Sengers, 1990) the authors took advantage of a linear relationship derived by Japas and Levelt Sengers (1989) for the asymptotic variation of Henry's constant near the solvent's critical point to construct a semiempirical correlation for aqueous Henry's constants. The form of the correlation was

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

where $k_H$ is the Henry's constant of solute 2 in solvent 1, defined by

$$k_H = \lim_{x_2 \to 0} (f_2/x_2) \tag{2}$$

$f_2$ is the fugacity and $x_2$ the liquid-phase mole fraction of the solute, $f_1^s$ is the fugacity of the solvent at saturation, $\rho_1^s$ is the saturated-liquid density and $\rho_{c,1}$ the critical density of the solvent, $T$ is the temperature in Kelvins, and $\tau$ is a constant which was fixed at 50 K.

The first two terms in Eq. 1 represent the linear relationship derived by Japas and Levelt Sengers (1989). As explained by Harvey and Levelt Sengers (1990), $A$ and $B$ can be related to infinite-dilution properties at the solvent's critical point. The final term with the $C$ parameter is an empirical correction effective at temperatures far from critical.

While Eq. 1 is successful in fitting Henry's constant data for solutes in water over a wide temperature range and in extrapolating to higher temperatures, it suffers from two shortcomings. First, the empirical correction term is specific to water as a solvent. Second, the correlation requires the evaluation of the density and fugacity of the solvent. Even for solvents such as water where reliable equations for these quantities are available, these calculations (particularly the fugacity; saturated liquid densities are frequently correlated as simple functions of temperature) are cumbersome, especially within applications such as process simulation where property calculations are repeated many times. An improved formulation would avoid the density and fugacity calculations, while preserving the high-temperature behavior given by the first two terms of Eq. 1. Also, we seek a three-parameter correlation; two parameters are simply not enough to fit Henry's constant data over a wide temperature range, but the data are seldom sufficient to justify four parameters.

The comparisons in Harvey and Levelt Sengers (1990) showed that, at least for nonpolar solutes in water, the best such simple three-parameter correlation in the literature was that of Krause and Benson (1989). Their equation took the form

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

where $T^* = T/T_{c,1}$ and $T_{c,1}$ is the solvent's critical temperature. The relative success of this equation was attributed to the fact that its second term yields a near-critical divergence nearly identical to that in the theoretically correct second term of Eq. 1. This is because the variation in the saturated density as the critical point is approached is related to the variation in temperature by the thermodynamic exponent $\beta$, defined by

$$|\rho_1^s - \rho_{c,1}| \sim |T - T_{c,1}|^\beta \tag{4}$$

The value of $\beta$ is $0.326 \pm 0.002$ (Sengers and Levelt Sengers, 1986). In reality, this asymptotic value is difficult to observe; experiments typically produce an "effective" $\beta$ near 0.355 (Levelt Sengers et al., 1976; Levelt Sengers and Sengers, 1981). Whether we consider the asymptotic exponent or an effective value, the Krause-Benson value of 1/3 is essentially correct with regard to the exponent associated with the critical divergence. Equation 3 is, however, not in full agreement with the limiting behavior of Eq. 1 because the temperature is taken to a different power and the pure-solvent fugacity is not included.

## New Correlation

Our objective is to recast Eq. 1 in a form requiring no density or fugacity evaluations. First, we note that the dominant term in the pure-solvent saturated fugacity is the solvent vapor pressure $P_1^s$, which can normally be calculated as a function of temperature from a simple correlating equation. Second, we substitute a temperature term like that of Krause and Benson (1989) for the term linear in density. Since we wish to cover a range of temperature larger than that in which the asymptotic exponent is manifested, we use the effective exponent $\beta = 0.355$. The result is

$$\ln k_H = \ln P_1^s + A/T^* + B(1-T^*)^{0.355}/T^* + f(C,T^*) \quad (5)$$

where we have used the reduced temperature $T^* = T/T_{c,1}$. The $A$ and $B$ terms reproduce the asymptotic behavior of Eq. 1; the final term is an empirical correction which should apply far from the critical temperature. The functional form of that term is arbitrary; we ask only that it have a single adjustable parameter and that it, like the other terms, be a function of temperature only. Several forms were tried; an exponential decay moderated by a power of reduced temperature worked best. The final form of the new correlation is

$$\ln k_H = \ln P_1^s + A/T^* + B(1-T^*)^{0.355}/T^* + C\exp(1-T^*)(T^*)^{-0.41} \quad (6)$$

## Results

Henry's constants were fitted to Eq. 6 for 13 solutes in water for which data are available over a wide range of temperature. The solvent vapor pressure $P_1^s$ for water was computed with the equation of Saul and Wagner (1987), and the critical temperature $T_{c,1}$ used was 647.14 K. The resulting parameters and information about the data sets are given in Table 1. For 10 of the solutes, the data used were identical to those used in Harvey and Levelt Sengers (1990). For carbon dioxide, the compilation of Crovetto (1991) was used. For ethylene, data came from several studies (Bradbury et al., 1952; Morrison and Billet, 1952; Davis and McKetta, 1960; Anthony and McKetta, 1967; Sanchez and Lentz, 1973). For hydrogen sulfide, low-temperature data were taken from the critical evaluation of Carroll and Mather (1989) and high-temperature data from Lee and Mather (1977) and Suleimenov and Krupp (1994). The data handling and fitting procedures were described by Harvey and Levelt Sengers.

In Table 2, the standard deviations in $\ln k_H$ are shown for the new correlation along with those for Eq. 1 (Harvey and Levelt Sengers, 1990) and Eq. 3 (Krause and Benson, 1989). Overall, Eq. 6 is as successful in fitting the data as the more computationally difficult equation of Harvey and Levelt Sengers. The equation of Krause and Benson also does well for most of the solutes, but is inferior for those ($H_2$, $N_2$, $O_2$, $CO_2$, $CH_4$) where the data extend to the highest temperatures. Figure 1 shows the fit of Eq. 6 to the data for four representative solutes.

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

| Solute | A | B | C | No. Pts. | Max. $T$ (K) |
|---|---|---|---|---|---|
| $H_2$ | −4.4964 | 6.0952 | 5.8390 | 42 | 636.13 |
| He | −3.6674 | 7.1476 | 4.5939 | 15 | 553.15 |
| Ne | −3.0496 | 5.4346 | 5.2244 | 13 | 543.4 |
| Ar | −7.4316 | 4.2239 | 9.6803 | 15 | 568.4 |
| Kr | −8.6850 | 3.6077 | 11.0380 | 12 | 525.6 |
| Xe | −13.3731 | 3.8360 | 14.9540 | 20 | 574.82 |
| $N_2$ | −11.6184 | 4.9266 | 13.3445 | 51 | 636.5 |
| $O_2$ | −9.4025 | 4.4923 | 11.3387 | 27 | 616.48 |
| $CO_2$ | −9.4234 | 4.0087 | 10.3199 | 60 | 631.7 |
| $H_2S$ | −5.7131 | 5.3727 | 5.4227 | 48 | 594.15 |
| $CH_4$ | −11.0094 | 4.8362 | 12.5220 | 38 | 633.15 |
| $C_2H_4$ | −11.5733 | 5.5672 | 11.9954 | 22 | 573.15 |
| $C_2H_6$ | −19.7237 | 4.5051 | 20.6740 | 20 | 473.5 |

Figure 2 illustrates, for nitrogen in water, the ability of Eq. 6 to extrapolate data to higher temperatures. To construct Figure 2, the correlation was re-fitted only to data below 450 K. Based on these limited data, Eq. 6 is able to predict the high-temperature Henry's constants well; this is a consequence of its functionality which minics the similarly successful Eq. 1 as the solvent's critical temperature is approached. Similarly good extrapolations are obtained for the other solutes.

To demonstrate the utility of Eq. 6 for nonaqueous solvents, the correlation was fitted to data (Cukor and Prausnitz, 1972; Chappelow and Prausnitz, 1974; Tremper and Prausnitz, 1976) for Henry's constants of 12 solutes in *n*-hexadecane at temperatures from 300 K to 475 K. The vapor pressure of hexadecane was taken from a recent DIPPR (1994) compilation, and the critical temperature used was 723 K. Figure 3 shows the results for ten of the solutes ($H_2S$ and HCl are omitted from the graph for clarity). Table 3 shows the coefficients and standard deviations in $\ln k_H$ from the fits, along with the standard deviations from fits to the equation of Krause and Benson (1989). For Eq. 6, the mean of the standard deviations is 0.0087, which is probably within the precision of the data. In contrast, the equation of Krause and Benson is worse for each of the solutes and has a mean standard deviation of 0.0282.

**Table 2. Standard Deviation in ln $k_H$ for Eq. 6 and Previous Correlations Applied to Solutes in Water**

| Solute | Eq. 6 | Krause and Benson (1989) | Harvey and Levelt Sengers (1990) |
|---|---|---|---|
| $H_2$ | 0.0412 | 0.0772 | 0.0484 |
| He | 0.0312 | 0.0254 | 0.0311 |
| Ne | 0.0260 | 0.0202 | 0.0261 |
| Ar | 0.0455 | 0.0399 | 0.0362 |
| Kr | 0.0424 | 0.0373 | 0.0278 |
| Xe | 0.0840 | 0.0791 | 0.0812 |
| $N_2$ | 0.0450 | 0.0960 | 0.0365 |
| $O_2$ | 0.0379 | 0.0583 | 0.0419 |
| $CO_2$ | 0.0407 | 0.0711 | 0.0510 |
| $H_2S$ | 0.0479 | 0.0529 | 0.0438 |
| $CH_4$ | 0.0447 | 0.0988 | 0.0477 |
| $C_2H_4$ | 0.0404 | 0.0406 | 0.0354 |
| $C_2H_6$ | 0.0246 | 0.0300 | 0.0486 |

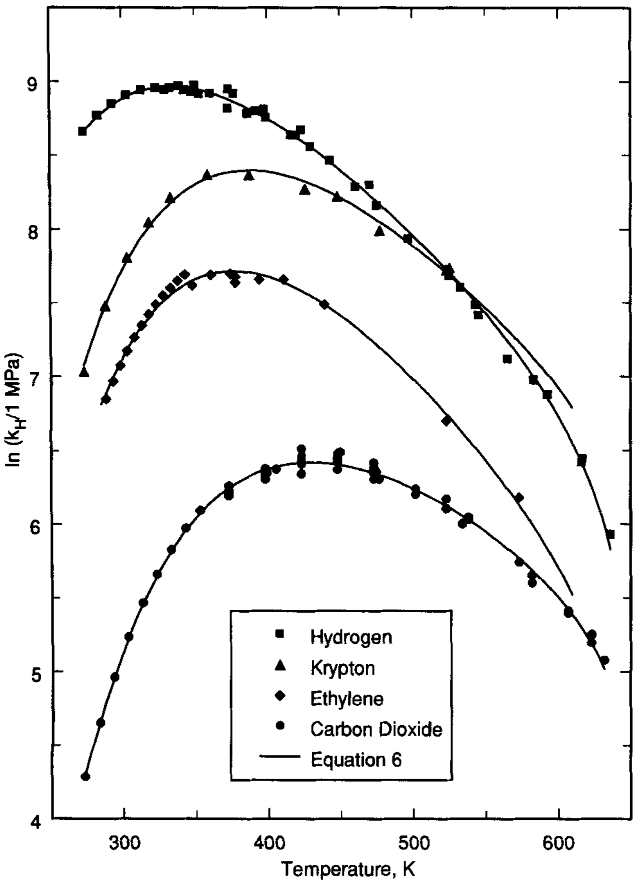

**Figure 1. Henry's constants for four solutes in water.**

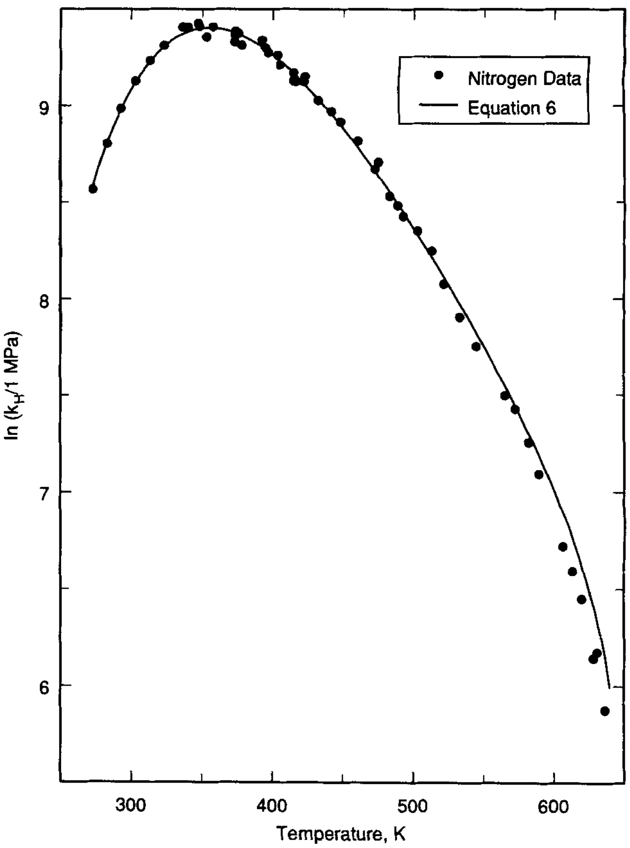

**Figure 2. Henry's constants for nitrogen in water.**

Extrapolation based on fit to data below 450 K.

## Discussion

For interpolation and smoothing of data over narrow temperature ranges, the selection of a fitting equation for Henry's constants is not particularly important (see Harvey and Levelt Sengers for discussion of the more common forms). However, if a wide temperature range is to be covered, and especially if data are to be extrapolated with confidence to higher temperatures, it is preferable to have an equation that behaves properly as the solvent's critical temperature is approached. Equation 6 incorporates this behavior in a way that avoids the computational disadvantages of Eq. 1, providing a tool that should be useful to engineers both for fitting data covering a large temperature range and for extrapolating data to higher temperatures.

After the publication of Harvey and Levelt Sengers (1990), it was discovered (Harvey et al., 1990) that the observed linear behavior of Henry's constant data according to the first two terms of Eq. 1 (in particular, the slope of the line) was probably not truly asymptotic. The asymptotic range is apparently not entered until the saturated-liquid density reaches about 1.5 times the critical density, which for water corresponds to a temperature about 7 K below the critical. The remarkable linearity of Eq. 1 is therefore more fortuitous than was first believed. Nevertheless, the data do obey that trend, and the utility of arranging the variables as in Eq. 1 (and therefore Eq. 6) is undeniable. The only caveat we would draw from the inconsistency in slopes is that these equations should not be extrapolated in temperature to within 1% or less of the solvent's critical temperature.

Another advantage of Eq. 6 is that it is not restricted to a specific solvent; all that is needed is the solvent's critical temperature and its vapor pressure curve. While the new correlating equation has not been tested exhaustively, the excellent results obtained for the very different solvents water and *n*-hexadecane suggest that it should be useful for Henry's constants in any solvent. A complete description of the fit to any system must include the critical temperature and vapor pressure correlation used for the solvent since these will influence the fit coefficients.

**Table 3. Parameters for Correlation of Henry's Constants in *n*-Hexadecane with Eq. 6**

| Solute | A | B | C | Std. Dev. in ln $k_H$ | Std. Dev. with Eq. 3 |
|---|---|---|---|---|---|
| $H_2$ | 10.3695 | 15.3496 | −13.8327 | 0.0102 | 0.0454 |
| HCl | 11.0640 | 13.1200 | −14.0102 | 0.0133 | 0.0281 |
| $N_2$ | 11.1293 | 14.7269 | −14.1939 | 0.0141 | 0.0313 |
| CO | 10.4926 | 14.6620 | −13.6984 | 0.0096 | 0.0329 |
| $CO_2$ | 9.7398 | 13.1263 | −12.5743 | 0.0077 | 0.0118 |
| $SO_2$ | 9.1034 | 12.3591 | −12.0053 | 0.0034 | 0.0138 |
| $H_2S$ | 10.9614 | 13.0533 | −14.0834 | 0.0035 | 0.0245 |
| $NH_3$ | 9.5758 | 13.1057 | −12.5946 | 0.0041 | 0.0115 |
| $CH_4$ | 10.1429 | 14.0998 | −13.3757 | 0.0029 | 0.0213 |
| $C_2H_6$ | 9.7549 | 12.5986 | −12.5758 | 0.0061 | 0.0188 |
| $C_3H_8$ | 10.2815 | 11.7436 | −12.8621 | 0.0022 | 0.0313 |
| $n$-$C_4H_{10}$ | 10.9729 | 10.7529 | −13.2064 | 0.0271 | 0.0675 |

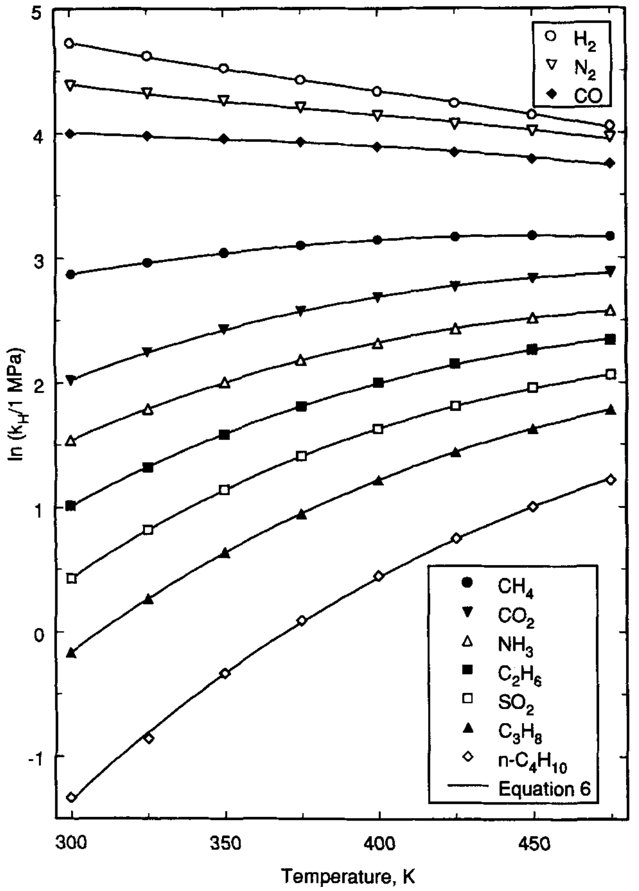

**Figure 3. Henry's constants for ten solutes in *n*-hexadecane.**

This correlation is intended for phase-equilibrium computations where the Henry's constant on the solvent's saturation curve is the quantity of interest. This allows Henry's constant to be expressed as a function of temperature only, since the pressure is implicitly the solvent's vapor pressure. If it is desired to compute derivative properties such as enthalpies of solution or partial molar volumes, Henry's constant (still defined by Eq. 2) must be described as a function of both temperature and pressure because the derivatives are taken in directions not parallel to the saturation curve. While little error will be introduced by taking straightforward temperature derivatives of Eq. 6 at low temperatures (where the change of pressure along the saturation curve is small), calculation of derivative properties at high temperatures requires a more complex formulation where temperature and pressure are independent variables. Such a formulation has been presented based on Eq. 1 (Harvey et al., 1991).

## Acknowledgments

The author thanks Rosa Crovetto for assistance with locating and interpreting aqueous Henry's constant data for carbon dioxide and ethylene, Alan Mather for assistance with aqueous hydrogen sulfide data and J. M. H. Levelt Sengers for helpful comments and discussion.

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*Manuscript received Apr. 24, 1995, and revision received July 6, 1995.*