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SOLUBILITIES OF GASES IN WATER AT HIGH TEMPERATURES

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SOLUBILITIES OF GASES IN WATER AT HIGH TEMPERATURES

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April 1981

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COMMUNICATION

Reliable solubility data for gases in water are scarce, especially at temperatures above 50°C. We present here a semi-empirical correlation of such solubilities based upon scaled-particle theory. The correlation applies to non-reactive gases at low pressures (where Henry's law holds) for the region 0 - 300°C. With this correlation, it is possible to make reliable estimates of solubilities at high temperature, provided that at least one experimental solubility is known at lower temperature, typically 25°C.

As discussed by several authors, notably Pierotti (1976) scaled-particle theory can be used to obtain an expression of Henry's constant for a solute (2) in solvent (1):

\[
\ln \frac{H_{2,1} V_1}{RT} = \frac{g_c}{RT} + \frac{g_1}{RT} \tag{1}
\]

where \( g_c \) is the work (Gibbs energy) required to make one mole of cavities in the solvent, where each cavity is sufficiently large to hold one molecule of solute; \( g_1 \) is the molar Gibbs energy of interaction between the solute in the cavity and the surrounding solvent molecules; \( R \) is the gas constant; \( T \) is the system temperature and \( v_1 \) is the molar volume of the solvent.

Henry's constant is defined by

\[
H_{2,1} = \lim_{x_2 \to 0} (f/x)_2 \tag{2}
\]

where \( f \) is the fugacity (essentially, the partial pressure) and \( x \) is the mole fraction.
Scaled-particle theory gives

$$\bar{\varepsilon}_c = K_0 + K_1 \sigma_{12}^2 + K_2 \sigma_{12}^2 + K_3 \sigma_{12}^3$$  (3)

where

$$K_0 = RT \left[ - \ln \left( \frac{1-\xi}{1} \right) + \frac{9}{2} \left( \frac{\xi}{1-\xi} \right)^2 \right] - N\eta P \sigma_1^3 / 6$$  (4)

$$K_1 = - \left( \frac{RT}{\sigma_1} \right) \left[ \frac{6\xi}{1-\xi} + 18 \left( \frac{\xi}{1-\xi} \right)^2 \right] + N\eta P \sigma_1^2$$  (5)

$$K_2 = \left( \frac{RT}{\sigma_1} \right) \left[ \left( \frac{12\xi}{1-\xi} \right) + 18 \left( \frac{\xi}{1-\xi} \right)^2 \right] - 2N\eta P \sigma_1$$  (6)

$$K_3 = \frac{4}{3} N\eta P$$  (7)

where reduced density $$\xi = n \sigma_1^3 \rho / 6$$; $$\rho$$ is the density per molecule; $$\sigma$$ is the molecular diameter and $$N$$ is Avogadro's number.

The total pressure is designated by $$P$$.

Following the procedure given by Wilhelm and Battino (1971), for a polar solvent (1) and a nonpolar solute (2)

$$\bar{\varepsilon}_d = \frac{4\pi \rho}{RT} \left[ \frac{8}{3} \varepsilon_{12} \sigma_{12}^6 - \mu_1^2 \sigma_{12}^2 \right]$$  (8)

where $$\mu$$ is the dipole moment, $$\sigma$$ is the polarizability, $$k$$ is Boltzmann's constant, and $$\varepsilon$$ is a parameter characterizing the strength of dispersion forces.

When Equations (1), (3) and (8) are used to calculate Henry's constants, results are sensitive to diameters $$\sigma_1$$ and $$\sigma_{12}$$ but not to parameter $$\varepsilon_{12}$$.

Pierotti (1975) studied the solubilities of gases in water at $$25^\circ C$$ and found that good results were obtained using

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}$$  (9)

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2)$$  (10)
with $\sigma_1 = 0.275$ nm and $\varepsilon_1/k = 85.3K$ for water.

We investigated solubility data for gases at higher temperatures. To do so, we required first, precise volumetric and vapor-pressure data for water; these are shown in Table 1. Second, we required reliable solubility data over a wide temperature range. These are scarce; we used data for argon (Benson and Krause 1976; Potter and Clynne 1978), carbon dioxide (Edwards et al 1978), helium (Wilhelm, Battino, Wilcock 1977; Pray et al 1952), hydrogen (Wilhelm, Battino, Wilcock 1977; Pray et al 1952), methane (Wilhelm, Battino, Wilcock 1977), neon (Benson and Krause 1976; Potter and Clynne 1978), nitrogen (Wilhelm, Battino, Wilcock 1977; Benson and Krause 1976; Pray et al, 1952), oxygen (Cramer 1980; Pray et al, 1952; Benson and Krause 1976) and xenon (Benson and Krause 1976; Potter and Clynne 1978).

We found that the experimental data could be fit well only if we allowed the key parameter $\sigma_{12}$ to be slightly dependent on temperature. For all gases studied here, that temperature dependence is given by

$$\sigma_{12} = \left(\frac{\sigma_1 + \sigma_2}{2}\right) F(T)$$  \hfill (11)

Where

$$F(T) = 16280 \left(\frac{1}{T}\right)^2 - 141.75 \left(\frac{1}{T}\right) + 1.2978$$  \hfill (12)

with $T$ in kelvins.

At $0^\circ$C, $F = 0.997$; at $300^\circ$C, $F = 1.10$.

Molecular parameters for 9 gases are given in Table 2. When Equations (11) and (12) are used, calculated Henry's constants are in good agreement with experiment as shown in Figures 1, 2 and 3. Here "good" means that the deviation between calculation and experiment is usually within $\pm 15\%$.

Deviations for helium are larger but there is good reason to question the reliability of the data. This is considered good because experimental uncertainties are large, especially for sparingly soluble gases at high temperatures.
calculated Henry's constants for 9 gases.

To estimate Henry's constants at high temperatures for a nonreactive gas not listed in Table 2, it is necessary to estimate first values of \( \sigma_2 \) and \( \epsilon_2 \). This can be done by utilizing one or more experimental Henry's constants at ambient temperatures. Since results are not sensitive to \( \epsilon_2 \), a rough estimate of \( \epsilon_2 \) (See for example, Hirschfelder, Curtiss and Bird 1954) is sufficient. Using the scaled-particle-theory equations given above, the experimental result(s) at ambient temperature(s) is (are) used to find \( \sigma_2 \). This value, utilizing Equations (11) and (12), can then serve to make calculations at high temperatures.

Figures 1, 2, and 3 show that Henry's constant is not a monotonic function of temperature. Therefore, simple extrapolation procedures (e.g. Hayduk and Laudie, 1973; Hayduk and Buckley 1971) may lead to large error. The semi-empirical procedure discussed here is likely to produce better results because the semi-theoretical basis provided by scaled-particle theory correctly reproduces the strongly non-linear variation of Henry's constant with temperature.

Scaled-particle theory for gas solubilities is necessarily limited to nonreactive gases; when applied to gases that react with water, calculated Henry's constants are too high. For example, aqueous solubility data for carbon monoxide (Wilhelm, Battino and Wilcock, 1977) are very well represented over the range 0-85°C using \( \sigma_2 = 0.395 \) nm and \( \epsilon_2/k = 134 \) K. When these parameters are used to calculate Henry's constants for carbon monoxide in the region 250-300°C, calculated results are about twice those measured by Jung et al (1971). However, these authors report appreciable chemical reaction between water and carbon monoxide at temperatures above 250°C, explaining the higher observed solubility.
While scaled-particle theory may provide a useful basis for correlating phase-equilibrium data, it is clear that there is a large gulf between the assumptions of the theory and the properties of real systems, especially aqueous systems. This gulf is partly absorbed in the adjustable parameters but at the cost of physical plausibility. It is strange, for example, that the best $\sigma_2$ for carbon dioxide (0.332 nm) should be smaller than the best $\sigma_2$ for carbon monoxide (0.395 nm). Scaled-particle theory is strongly sensitive to the value of $\sigma_2$; therefore, it is important to evaluate this parameter carefully from reliable experimental data, while recognizing that its physical significance is only approximate.

Acknowledgment

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Berkeley, CA 94720
Literature Cited

Hirschfelder, J.O., Curtiss, C.F. and Bird, R.B.
### Table 1

Saturated Densities and Vapor Pressures for Water

<table>
<thead>
<tr>
<th>$t$, °C</th>
<th>$v$, cm³/g</th>
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<tr>
<td>0</td>
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# from Steam Tables 1964

Department of Scientific and Industrial Research
National Engineering Laboratory, Edinburgh
Her Majesty's Stationery Office
### Table 2

**Scaled-Particle-Theory Parameters for Calculation of Henry's Constants**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \sigma_{\text{nm}} )</th>
<th>( \frac{\varkappa}{k} ), K</th>
<th>( 10^{24} \bar{\lambda}, \frac{\text{cm}^3}{\text{molecule}} )</th>
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<td>Xenon</td>
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\[ \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} \]

Dipole moment of water = 1.84 Debye
Table 3

Calculated Henry's Constants, $10^{-3}$ bar

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<tr>
<th>$t$, °C</th>
<th>Argon</th>
<th>Carbon Dioxide</th>
<th>Helium</th>
<th>Hydrogen</th>
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CALCULATED AND OBSERVED HENRY'S CONSTANTS (BAR)

Figure 1
CALCULATED AND OBSERVED HENRY'S CONSTANTS (BAR)

Figure 2
Figure 3

CALCULATED AND OBSERVED
HENRY'S CONSTANTS (BAR)
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