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SOLUBILITIES OF GASES IN WATER AT HIGH TEMPERATURES

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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):

$$\ln \frac{H_{2,1} v_1}{RT} = \frac{\bar{g}_c}{RT} + \frac{\bar{g}_1}{RT} \quad (1)$$

where $\bar{g}_c$ 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; $\bar{g}_1$ 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

$$H_{2,1} = \lim_{x_2 \rightarrow 0} (f/x)_2 \quad (2)$$

where f is the fugacity (essentially, the partial pressure) and x is the mole fraction.

Scaled-particle theory gives

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

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

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

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

$$K_3 = 4/3 N\pi P \quad (7)$$

where reduced density $\xi = \pi \sigma_1^3 \rho/6$; ρ is the density per molecule; σ 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)

$$\frac{\bar{g}_1}{RT} = \frac{4\pi\rho}{3kT \sigma_{12}^3} \left[\frac{8}{3} \epsilon_{12} \sigma_{12}^6 - \mu_1^2 \alpha_2 \right] \quad (8)$$

where μ is the dipole moment, α is the polarizability, k is Boltzmann's constant, and ϵ 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 σ_1 and σ_{12} but not to parameter ϵ_{12} .

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

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \quad (9)$$

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2) \quad (10)$$

with $\sigma_1 = 0.275$ nm and $\epsilon_1/k = 85.3K$ 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 σ_{12} to be slightly dependent on temperature. For all gases studied here, that temperature dependence is given by

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

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

with T in kelvins.

At 0°C , $F = 0.997$; at 300°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. Table 3 gives

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 σ_2 and ϵ_2 . This can be done by utilizing one or more experimental Henry's constants at ambient temperatures. Since results are not sensitive to ϵ_2 , a rough estimate of ϵ_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 σ_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 σ_2 for carbon dioxide (0.332 nm) should be smaller than the best σ_2 for carbon monoxide (0.395 nm). Scaled-particle theory is strongly sensitive to the value of σ_2 ; therefore, it is important to evaluate this parameter carefully from reliable experimental data, while recognizing that its physical significance is only approximate.

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Table 1

Saturated Densities and Vapor Pressures for Water [#]

t, °C	v, cm ³ /g	p ^{sat} , bar
0	1.0002	0.00611
10	1.0003	0.01227
20	1.0018	0.02337
25	1.0030	0.03166
50	1.0121	0.12335
75	1.0258	0.38547
100	1.0435	1.01330
125	1.0649	2.32090
150	1.0906	4.75974
175	1.1208	8.92471
200	1.1565	15.5514
225	1.1992	25.5045
250	1.2512	39.7762
275	1.3168	59.4869
300	1.4036	85.9196

[#] from Steam Tables 1964

Department of Scientific and Industrial Research

National Engineering Laboratory, Edinburgh

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

Fluid	σ, nm	$\frac{\epsilon}{k}, \text{K}$	$10^{24} \alpha, \frac{\text{cm}^3}{\text{molecule}}$
Water	0.275	85.3	1.590
Argon	0.356	122.0	1.630
Carbon Dioxide	0.332	300.0	2.590
Helium	0.264	2.0	0.204
Hydrogen	0.267	10.0	0.802
Methane	0.413	160.0	2.700
Neon	0.309	34.9	0.393
Nitrogen	0.373	95.0	1.730
Oxygen	0.362	118.0	1.560
Xenon	0.432	221.0	4.100

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \quad \text{dipole moment of water} = 1.84 \text{ Debye}$$

Table 3

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

t, °C	Argon	Carbon Dioxide	Helium	Hydrogen	Methane	Neon	Nitrogen	Oxygen	Xenon
0	25.9	1.19	120.0	58.0	23.9	99.6	59.7	32.1	6.43
10	31.0	1.52	127.0	62.7	30.4	109.0	70.9	38.3	8.69
20	35.8	1.88	131.0	66.6	37.1	117.0	81.4	44.2	11.20
25	38.1	2.23	133.0	68.2	40.4	120.0	86.2	47.0	12.50
50	48.1	3.08	135.0	73.6	56.0	130.0	106.0	59.0	19.50
75	54.7	4.09	130.0	74.8	67.7	131.0	118.0	66.7	26.00
100	57.6	4.99	120.0	72.7	73.9	125.0	120.0	69.5	30.80
125	57.1	5.70	108.0	68.1	74.9	115.0	115.0	68.4	33.40
150	53.9	6.17	94.7	61.9	71.1	101.0	105.0	63.9	33.80
175	48.8	6.40	81.0	54.7	64.3	86.9	91.6	57.3	32.20
200	42.7	6.38	67.8	47.3	55.6	72.7	77.2	49.6	29.30
225	36.1	6.15	55.5	39.8	46.2	59.2	62.8	41.5	25.40
250	29.5	5.74	44.3	32.7	36.9	46.8	49.3	33.6	21.10
275	23.3	5.17	34.3	26.0	28.1	35.8	37.2	26.2	16.80
300	17.5	4.48	25.5	19.8	20.4	26.2	26.6	19.4	12.70

CALCULATED AND OBSERVED HENRY'S CONSTANTS
(BAR)

Figure 1

CALCULATED AND OBSERVED
HENRY'S CONSTANTS (BAR)

Figure 2

CALCULATED AND OBSERVED
HENRY'S CONSTANTS (BAR)

Figure 3

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