A Critical Evaluation of the Solubility of Simple Inorganic Gases in Water at High Temperature

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The knowledge of the temperature dependence of the solubility of simple gases in water over a wide temperature range is of great importance for solution physical chemistry, as well as for chemical engineering and geothermal processes. The present work is particularly concerned with temperatures above the normal boiling point of water.

Since Himmelblau's (1960) review of gas solubility data in water at high temperatures, new experimental studies have been published. The two more recent articles in which solubility data for gases in water at high temperature have been assessed (Clever and Han, 1980; Schultze and Prausnitz, 1981) do not include all the experimental results available now. Furthermore, the nonideal behavior of the gas phase in equilibrium with the solution, which becomes more important as the temperature increases (i.e., as the solvent partial pressure increases) (Crovetto et al., 1982), has not been considered properly in previous work. In order to be able to use results from various authors obtained under different experimental conditions to establish the temperature dependence of Henry's constants, it is necessary to reevaluate the data of the different sources before they may be processed together.

For the binary systems we are interested in, i.e., simple nonreactive gaseous solutes in liquid solvents, the thermodynamic description of the liquid-vapor equilibrium is given in terms of Henry's constant by the following expressions (O'Connell, 1977; Crovetto et al., 1983):

$$1 - y = \frac{(1 - x)P_1^0\Phi_1^0 \exp\{v_1(P - P_1^0)/RT\}}{P\Phi_1}$$

$$k_H^0 = \frac{yP\Phi_2}{x}\exp\{-v_2^\infty(P - P_1^0)/RT\} = k_H \exp\{-v_2^\infty(P - P_1^0)/RT\} \tag{1}$$

The liquid phase activity coefficients have been assumed unity because the saturated solutions of gases are sufficiently dilute.

Practically all the experimental studies of gas solubilities in water at high temperature have only determined the composition of the liquid phase (x) in equilibrium. In order to calculate k_H^0 from x, P and T, nonideal behavior has either been altogether ignored, hence making

$$k_H = \frac{(P - P_1^0)}{x} \tag{2}$$

or deviation from ideal behavior were taken into account through the correction of the solute pressure with the Φ_2 value obtained with Lewis and Randall's rule; i.e., making the product $P_2\Phi_2$ equal to the fugacity of the pure gaseous solute at (P,T) times the mole fraction of the solute in the gas phase. In this case, Henry's constant is given by

$$k_H = \frac{(P - P_1^0)\Phi_2^0}{x} \tag{3}$$

However, Eq. 3 does not take account of the effect that the nonideal behavior on the gaseous mixture has in changing the composition of the gas phase. It is interesting to note that k_H calculated with Eq. 3 is found to differ more from the correct Henry's constant than that obtained with Eq. 2, because the assumption made by Lewis and Randall's rule is very poor for water-nonpolar gas mixtures and also because, to a first approximation, the difference from unity of the fugacity coefficient is partially compensated by the change of composition in the gas phase.

Henry's constants were calculated with Eq. 1 employing a second virial coefficient equation of state for the gas phase mixture with gas density as variable. The cross second virial coefficients describing H_2O–nonpolar gas interactions were obtained following the method of Rigby et al. (1969). This procedure was found satisfactory up to 629 K and for solute partial pressures not exceeding 30 MPa. The effect of nonideality was found to introduce changes in y and Φ_2 of up to 20 to 40%, respectively.

It was considered important to test the method of calculation that has been adopted in this work. The best way of doing this consists in comparing calculated gas phase compositions with experimental values. The only data found in the literature for the systems and conditions met in this work are for the nitrogen-water mixture. Figure 1 shows that the values calculated with Eq. 1 agree very well

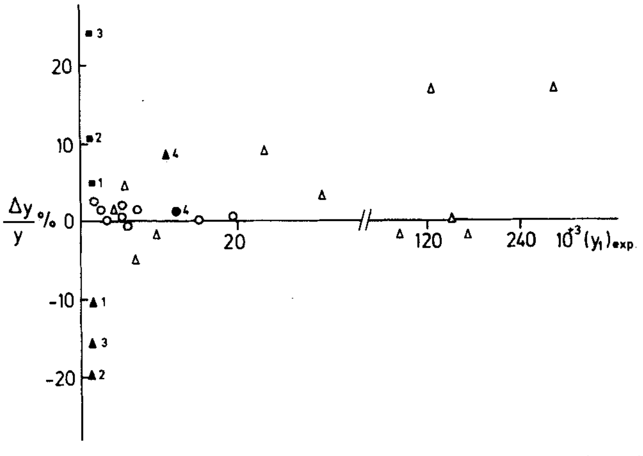

Figure 1. Relative deviations between predicted and experimental values of the mole fraction of water in the gas phase (y_1) for the N_2-H_2O system. ○: Peng, D.-Y., and D. B. Robinson, "Two- and Three-Phase Equilibrium Calculations for Coal Gasification and Related Processes," *Thermod. Aq. Syst. Ind. Appl.*, Ed., S. A. Newman, ACS Symp. Ser. 133, p. 393 (1980). △: Saddington, A., and N. W. Krase, "Vapor-Liquid Equilibria in the System Nitrogen-Water," *J. Amer. Chem. Soc.*, 56, 353 (1934). □: Bartlett, E. P., "Vapor in Compressed Hydrogen, Nitrogen and a Mixture of these Gases in the Presence of Condensed Water," *J. Amer. Chem. Soc.*, 49, 65 (1927). ■●▲: Indicate points at same (P,T) for two of the sources: (1) (323 K, 10 MPa); (2) (323 K, 20 MPa); (3) (323 K, 30 MPa); (4) (373 K, 10 MPa).

with the experimental ones. The discrepancies between calculated and experimental y observed for some points are due to experimental uncertainty in the determination of the gas phase composition. This is clearly illustrated by the full symbols in Figure 1, which denote y values reported by two different sources of data corresponding to precisely the same (P,T) condition and consequently should have the same experimental value for y. It may be noted that in all cases making $y = (P - P_1^0)/P$ gives much greater discrepancy with experiment than with the y value calculated with Eq. 1. The agreement observed in Figure 1 is encouraging as regards the consistency of Eq. 1 with a second virial coefficient equation of state in describing the thermodynamics of the water–nonpolar gas binary systems. Furthermore, Figure 1 gives evidence to support the view that gas phase compositions are liable to great experimental uncertainties.

In order to apply Eq. 1 to all the data in the literature, it was found necessary to recover the experimental P against x set of values for each temperature, so that one can then deal with all the data in the same consistent way. Since many authors do not report the total pressure, we had to generate the set of "raw" data by inverting the calculation indicated by each individual author so as not to introduce additional uncertainty by the recalculation. The data requiring this procedure are identified in Table 1.

All the information on gas solubilities in water at high temperatures available in the literature has been surveyed. However, our numerical analysis only included those that were presented in tabular form. Table 1 identifies the sources surveyed and those that were finally included in the numerical evaluation. In many instances only average values for $\ln(k_H)$ may be reported, since it was found either that the slope of the curve of $\ln(k_H)$ against $(P - P_1^0)$ was very small or even slightly negative, or that the scatter of experimental points was such that there was great uncertainty in the extrapolated value. Clearly, with two exceptions, the pressure dependence of k_H is greatly influenced by experimental artifacts, because the observed slopes give values of v_2^∞ that differ very much among various authors and in some cases even give physically meaningless values. Consequently, the values of the solute's partial molar volumes obtained from the pressure dependence of Henry's constants are found to be generally unreliable.

For some high-quality sets of data restricted to temperatures not higher than about 373 K, we have considered also solubility data reported for temperatures down to 323 K. This proved to be important since these are the sets of data that bridge the low temperature region where very precise gas solubility data exist (Wilhelm et al., 1977), with the high temperature region we are interested in, and thus enabled a better analysis for some of the gas-water systems.

The complete sets of data for each gas-water binary system were

TABLE 1. SOURCES OF SOLUBILITY OF GASES IN WATER SURVEYED IN THE PRESENT STUDY

Systems	Sources
He-H_2O	W35, P52, S62, G72, P78
Ne-H_2O	P78, C82
Ar-H_2O	P78, C82
Kr-H_2O	P78, C82
Xe-H_2O	S56, P78, C82
H_2-H_2O	W34, I34, S51, B52, P52, S56
N_2-H_2O	G31, W33, S34, S51, P52, O70, S76
O_2-H_2O	P52, P53a, Z54, S56, B71, B78, C82a

G31: Goodman, J. B. and N. W. Krase, "Solubility of Nitrogen in Water at High Pressures and Temperatures," *Ind. Eng. Chem.*, **23**, 401 (1931).
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[1] Data presented only in graphical form, not included in this work.
[2] Pressure variable has been recalculated (cf. text).
[3] Solubility of He at 373 K could not be used because there is internal inconsistency between calculated and reported value of k_H^0.

TABLE 2. COEFFICIENTS OF THE EQUATION

$$\ln(k_H^0/GPa) = A + \frac{10^3 B}{(T/K)} + \frac{10^6 C}{(T/K)^2} + \frac{10^9 D}{(T/K)^3}$$

	a	b	A	B	C	D	T_M/K	$\ln(k_H^0 GPa)_M$	σ
He-H_2O	13	5	−7.1950	6.0041	−0.9164	$0.1617.10^{-2}$	302.6	2.697	0.072
Ne-H_2O	12	2	−8.4334	8.3778	−1.9423	0.1245	329.6	2.584	0.024
Ar-H_2O	22	2	−10.1928	9.6808	−2.2418	0.1151	365.6	1.870	0.013
Kr-H_2O	9	2	−6.6684	6.0225	−1.0342	$-2.838.10^{-2}$	380.6	1.478	0.028
Xe-H_2O	15	3	−14.5622	13.8663	−3.6512	0.2491	387.5	1.187	0.12
H_2-H_2O	14	4	−11.9767	12.0615	−3.3332	0.2902	340.4	2.061	0.154
O_2-H_2O	22	4	−16.8297	16.8494	−4.7347	0.3987	370.3	1.994	0.073
N_2-H_2O	14	5	−17.2531	17.9056	−5.1346	0.4526	366.7	2.571	0.060

a = number of data points included in the study of the temperature dependence of k_H^0.
b = number of original sources of the data. σ = standard deviation.
Notes: He-H_2O: Only two points exceeded 1.5σ; if they were eliminated, two new points deviating that much appeared. Ne-H_2O: this difficult set was analyzed in three ways: one P78 datum and all C82, all data from P78 and only two C82, and all the data points. The smallest standard deviation corresponds to the first way, so this was accepted (eight final points considered). Ar-H_2O: four points were eliminated because they scattered more than 1.7σ; other three corresponding to temperatures lower than 340 K, were eliminated because they deviate more than 1σ from the low temperature behavior as described by Wilhelm et al. (1977). Kr-H_2O: One point from P78 was eliminated because it scattered more than 1.9σ. Xe-H_2O: There are three points scattering more than 1.5σ; nevertheless their elimination worsens the fitting; all points were considered. H_2-H_2O: All points used in spite of large scatter found for some points; no criterion to select among the sets of data ppears to be valid. N_2-H_2O: One point eliminated because it scattered more than 2.1σ.

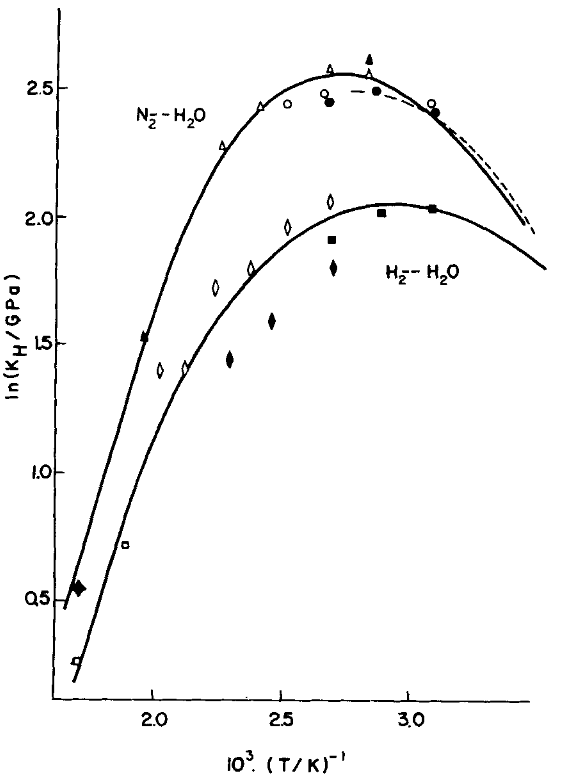

Figure 2. Plot of $\ln(k_H^0)$ against $(1/T)$ for H_2-H_2O system and for N_2-H_2O system. Solid curves correspond to polynomial expressions reported in Table 2; dashed curve corresponds to polynomial expression given by Wilhelm et al. (1977) from solubility data in low temperature region. H_2-H_2O: ■, W34; ◇, I34; ♦, S56; □, P52. N_2-H_2O: ○, O70; ●, W33; △, G31; ▲, S34; ★, P52.

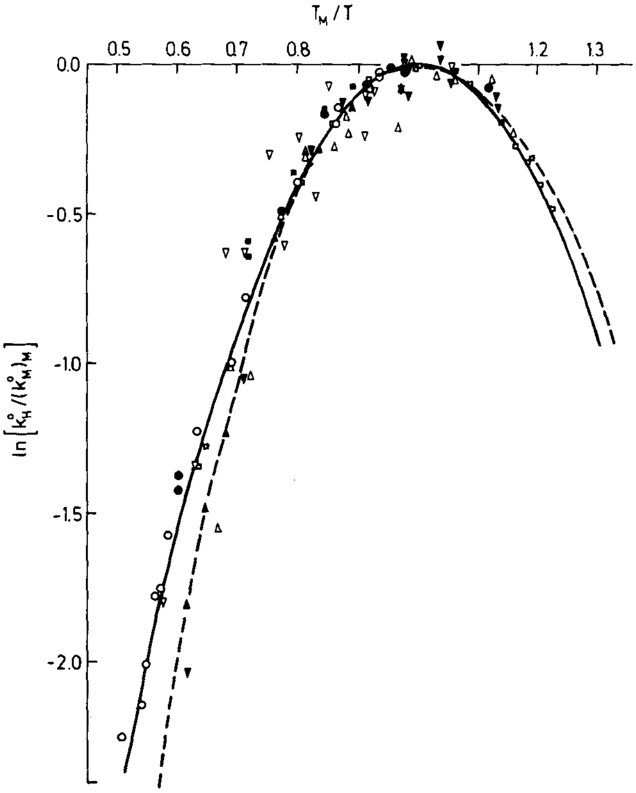

Figure 3. The solid curve is a plot of Eq. 5 against reduced temperature; the dashed curve represents the equation of Himmelblau (1960). All the data points covered in this study are shown: ○, He; ●, Ne; □, Ar; ■, Kr; △, Xe; ▲, O_2; ▽, H_2; ▼, N_2.

fitted to polynomials in powers of the reciprocal temperature (Crovetto et al., 1982) of the form

$$\ln(k_H^0/GPa) = A + \frac{10^3B}{(T/K)} + \frac{10^6C}{(T/K)^2} + \frac{10^9D}{(T/K)^3} \qquad (4)$$

For each binary system, the polynomial, Eq. 4, was required to pass through the values of $\ln(k_H^0/GPa)$ corresponding to the temperatures of 278.2 and 322.2 K given by the equations obtained by Wilhelm et al. (1977) in their critical survey of the most precise available data for gas solubilities in water at low temperature.

Table 2 reports the values found for the coefficients of Eq. 4 for each binary system. Experimental points were eliminated from the fitting procedure whenever they scattered badly from the rest of the data and if their elimination improved substantially the fit to Eq. 4. Details are given at the bottom of Table 2.

For the systems O_2-, H_2- and N_2-H_2O, which are of great practical importance, severe discrepancies are found among the different sources of data. This is illustrated for the two latter systems in Figure 2. The same may be said of the Xe-H_2O and, to a lesser extent, of the He-H_2O systems. No statistical test of the data was found adequate to decide on the relative quality of the various available sets of data. It is clear that more experimental work is necessary to establish on a firmer basis the behavior of the diatomic gases in water, which are of so great practical importance, as well as that of Xe in H_2O.

Himmelblau (1960) proposed an equation in terms of reduced variables having four adjustable coefficients that gave the temperature dependence of the solubility of all the gases he studied in water. We have employed the much simpler equation

$$\ln(k_H^0/(k_H^0)_M) = -a\left(\frac{T_M}{T} - 1\right)^2 \qquad (5)$$

Equation 5 has a single adjustable coefficient for all the gas-water systems; its best value was found to be $a = 10.081$. With this value it is possible to describe with Eq. 5 all the solubility data in the temperature range 278 to 600 K with a standard deviation in k_H^0 smaller than 20%. This is quite remarkable for such a simple equation, which thus becomes of great practical interest. Figure 3 shows the performance of Eq. 5 and compares it with that of Himmelblau (1960).

It seems that a more accurate description of gas solubilities in water is not required at present because Eq. 5 works well in the temperature range for which data are available. Furthermore, the standard deviation of the data with respect to Eq. 5 is not much greater than that observed for those systems that scatter more severely from Eq. 4.

The possibility of having a simple expression to describe the behavior of binary systems consisting of a simple inorganic gas and water over a wide temperature range is of great practical importance in design and operation of many chemical engineering processes. In the case of the power industry, this knowledge is of interest for those power generating plants that make use of the water-steam cycle, as well as for application to processes occurring in the primary circuits of nuclear power plants of the PWR type.

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NOTATION

k_H = Henry's constant, $= f(P,T)$
k_H^0 = Henry's constant for zero solute partial pressure, $= f(T)$
$(k_H^0)_M$ = Henry's constant corresponding to the temperature of minimum solubility
P = total pressure
P_i = partial pressure of component i
R = gas constant
T = absolute temperature
T_M = temperature of minimum solubility
v_i = partial molar volume of component i
x = mole fraction of the solute gas in the liquid phase
y = mole fraction of the solute gas in the gas phase
Φ_i = fugacity coefficient of component i
^{o} = pure component
∞ = infinite dilution
1,2 = water and gaseous solute, respectively

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Turbulent Mixing in Tubes with Transverse Injection

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One of the simplest flows of confined turbulent mixing is a small transverse jet into a tube or pipe. This flow is also attractive as it is a common flow element in technology. A transverse jet at $x = 0$ introduces one fluid into the tube and at the same time injects vorticity from the nonconservative force on the axial flow in the tube. The circulation of the vorticity stirs the two fluids together. As time elapses, or correspondingly as the downstream distance increases, the magnitude of the concentration fluctuations declines. Although the fluctuations may never be exactly zero, after they reach some low value, say, 1 percent of the mean concentration, the two fluids are practically a homogeneous mixture. In many technical applications it is desirable that the mixing occur as rapidly as possible. Hence the rate of decay of the fluctuations is a useful measure of the mixing efficacy of the turbulence.

CONCENTRATION FLUCTUATION MEASUREMENTS

An aspirating probe, initially developed by Brown and Rebollo (1972), was used to measure the concentration fluctuations between two streams of gas, one of helium and the other nitrogen. Probe spatial resolution was approximately 0.1 cm. The tube inside diameter D was 2.3 cm. The transverse jet flowed through a sharp-edged hole, which was 0.1, 0.2, and 0.4 cm during the course of the experiments.

Typical Reynolds numbers are about 10^3 for the tube flow and 10^4 for the transverse jet. A porous metal plug of 40 μ pore size was positioned in the tube 3 diam. upstream of the transverse jet to generate a uniform nitrogen velocity in the tube.

Typical results are shown in Figure 1. The fluctuations, normalized by the mean concentration of the mixture, are plotted as a function of downstream distance normalized by tube diameter D for several values of the ratio of transverse to axial momentum J. For incompressible flow, as was the case here

$$J \equiv \frac{\rho_j V_j^2 A_j}{\rho U^2 A}$$

where ρ_j, V_j, and A_j are the jet density, velocity, and area at the nozzle exit. The corresponding tube quantities are ρ, U, and A. An orifice coefficient of 0.8 was assumed for all the jet orifices.

The fluctuations decline in Figure 1 approximately as $(x/D)^{-1}$ for almost all values of J tested. Figure 2 illustrates the dependence on J at a fixed downstream station. Except at very small and very large J, the fluctuations vary as J^{-1}. Also, the fluctuations seem to be independent of the jet diameter d, except perhaps at large J.

Although the radial position of the probe was changed within the tube, no transverse variation in c' was observed, except for the case of anemic jets where $J < 0.1$.

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