Solubilities of Inert Gases in Water

0° C. to Near the Critical Point of Water

D. M. HIMMELBLAU, Department of Chemical Engineering,
The University of Texas, Austin, Tex.

THE SOLUBILITY of gases in water is of considerable industrial and theoretical importance; a vast amount of experimental work has been done, and a variety of behavior found. There are so many aspects to solubility problems—the effect of temperature, pressure, association, dissociation, and type of solvent, among others—that this study had to be limited to the effect of temperature on solubility. The gases chosen do not react with water nor ionize or dissociate in water. To avoid considering systems which form multiple liquid phases at high pressures and have large deviations from ideality at low pressures, only gases whose critical temperatures were below the freezing point of water were studied: oxygen, nitrogen, hydrogen, helium, xenon, and methane.

Research into the solubility of gases in water can be traced as far back as the work of Henry (*5*) in the year 1803. An extensive amount of literature is available on the solubility of oxygen, nitrogen, hydrogen, helium, xenon, and methane in the vicinity of room temperature, and a moderate amount of data can be found for temperatures up to the normal boiling point of water. Only recently, some data have become available on the solubility of gases at high temperatures. Early workers in the field realized that some gases exhibited a solubility minimum with respect to temperature, and that the correlation of solubility data as a function of temperature was not simple. Previous theories correlating solubility or attempting to explain gas solubility have been of limited use because they have not been able to take advantage of this recent high temperature data. A correlation of the solubility of these gases as a function of temperature would be of considerable theoretical as well as industrial significance.

SOLUBILITY EXPRESSIONS

Solubility data have been reported on a number of more or less well known bases, such as the coefficients of Henry, Bunsen, Ostwald, Raoult, and Kuenen. Any attempt to correlate solubility data should be based on a sound theoretical approach which could easily be translated into a practical system for direct use of the data.

The ideal solution, like the ideal gas, is a convenient fiction approached by some actual solutions. While inert gases which are not readily soluble in water do not follow Raoult's law (the fugacity of the gas over the solution equals the fugacity of the pure component at the temperature and pressure of the solution times the mole fraction), Henry's law substitutes an arbitrary fugacity for the fugacity of the of the pure component to say

$$p\nu = f = f'(x)(\Phi) = H(x)(\Phi) \tag{1}$$

where

f = the fugacity of the solute gas in the vapor phase
f' = H = Henry's law constant
x = mole fraction of the solute gas in the liquid phase
Φ = activity coefficient of the solute gas in the liquid phase; Φ = 1.00 at the standard state of infinite dilution
ν = activity coefficient of the solute gas in the vapor phase; ν = 1.00 at zero pressure

For inert gases which obey the ideal gas law in the vapor phase above the solution—i.e., at low pressures—Equation 1 becomes the familiar

$$p = H(x) \tag{2}$$

where p = partial pressure of solute gas in the vapor phase.

Inasmuch as the Henry's law constant for slightly soluble gases can easily be changed to other commonly used expressions for solubility, all the data are reported here as Henry's law constants. Equations for transforming H into other solubility relations are discussed by Markham and Kobe (*10*) and Friend and Adler (*2*), and are repeated in compact form below for slightly soluble gases for convenience. Some of these equations are not exact, but they give values within 0.1% of the exact values of the coefficients. H is expressed in atmospheres per mole fraction.

Kuenen coefficient: $S \left(\frac{\text{cc. of gas at S.T.P.}}{\text{g. } H_2O}\right)$

$$S = \frac{1244}{H} \tag{3}$$

Bunsen coefficient: $\alpha \left(\frac{\text{cc. of gas at S.T.P.}}{\text{cc. } H_2O}\right)$

$$\alpha = \frac{1244(\rho)}{H} \tag{4}$$

where ρ = density of solvent at temperature, T

Ostwald coefficient: $l \left(\frac{\text{cc. of gas at } T}{\text{cc. of } H_2O \text{ at } T}\right)$

$$l = \frac{1244(\rho)}{H}\left(\frac{T}{273}\right) \tag{5}$$

where T = temperature, ° K., and ρ = density of solvent at T.

AVAILABLE HIGH TEMPERATURE SOLUBILITY DATA

Extensive solubility data below 100° C. can be found in standard reference books and review articles (*3, 5, 8-10, 12, 13, 19-21, 28*).

Most of the pertinent measurements of gas solubility at temperatures above the normal boiling point of water have been made at the Battelle Memorial Institute (*14-17, 23*). Morrison and Johnstone (*12*) and Weibe and Gaddy (*25-27*) have made extensive studies of gas solubility in water at temperatures from 0° to 100° C., or slightly above. High temperature solubility of methane has been reported by Culbertson and McKetta (*1*) and Michels (*11*). A large, but not exhaustive number of other references for oxygen, nitrogen, hydrogen, helium, xenon, and methane at temperatures above 100° C. are given in Table I with the approximate temperature range of the recorded data.

All high pressure data were extrapolated to low pressures so that only the influence of temperature on the Henry's law constant had to be considered. Such a mass of data is avail-

Table I. References for Solubility of Gases in Water at Elevated Temperatures

Gas	Lit. Ref.	Year	Temperature Range	
			° C.	° F.
O_2	(*14*)	1952	163-343	325 650
	(*15*)	1953	100-163	212-325
	(*29*)	1954	0-330	32-625
	(*23*)	1956	100-288	212-550
N_2	(*4*)	1931	0-169	32-338
	(*18*)	1934	50-240	122-464
	(*22*)	1951	76-240	169-464
	(*24*)	1951	66-302	150-575
	(*14*)	1952	25-316	77-600
H_2	(*24*)	1951	66-332	150-630
	(*14*)	1952	163-316	325-600
	(*16*)	1953	100-163	212-325
	(*23*)	1956	100-163	212-325
He	(*14*)	1952	333-316	167-600
	(*23*)	1956	163-302	325-575
Xe	(*23*)	1956	100-302	212-575
CH_4	(*11*)	1936	25-150	77-302
	(*1*)	1951	25-171	77-340

able that it was necessary to reconcile apparent inconsistencies or discard apparently erroneous data before any attempt could be made to correlate this material.

CORRELATION OF SOLUBILITY DATA

Some of the most consistent and accurate data in the literature seemed to be completely at odds with the work of other investigators whose results standing alone appeared equally reliable.

By plotting the logarithm of the Henry's law constant *vs.* the inverse of the absolute temperature rather than the standard technique of reporting "milliliters of gas at standard temperature and pressure per 100 grams of water" as a direct function of temperature (utilizing a third parameter of pressure), the discrepancies among the results of the investigators listed in Table I became clearer. Experimental errors with a consistent bias were thus more easily spotted. An additional reason for plotting ln H *vs.* $1/T$ is that theoretically

$$\frac{\partial(\ln H)}{\partial\left(\frac{1}{T}\right)} = - \frac{\bar{H}_2^* - \bar{H}_2^\circ}{R} \tag{6}$$

where

$\bar{H}_2^*$ = the partial molal enthalpy of the gas in the ideal state at T

$\bar{H}_2^\circ$ = the partial molal enthalpy of the gas in an infinite dilute solution at T

R = the universal gas constant

Equation 6 represents the molal heat of dissolution (divided by R) of gas from an infinitely dilute solution to the ideal gas state at temperature T.

After examining all the available high temperature solubility data of the gases by means of various types of plots, the data in the following references were excluded from the data used in this correlation for three reasons:

Not enough information reported to calculate H [(*24*) for N_2 and H_2].

Identical data repeated in a later publication [(*14*) for He and (*15*) for O_2].

Data at wide variance with that of other workers [(*14*) for H_2 and (*4*) for N_2].

The remaining data are presented in Figures 1 and 2. Additional data for temperatures below 100° C. were obtained from Seidell (*19-21*) for the most reliable investigators.

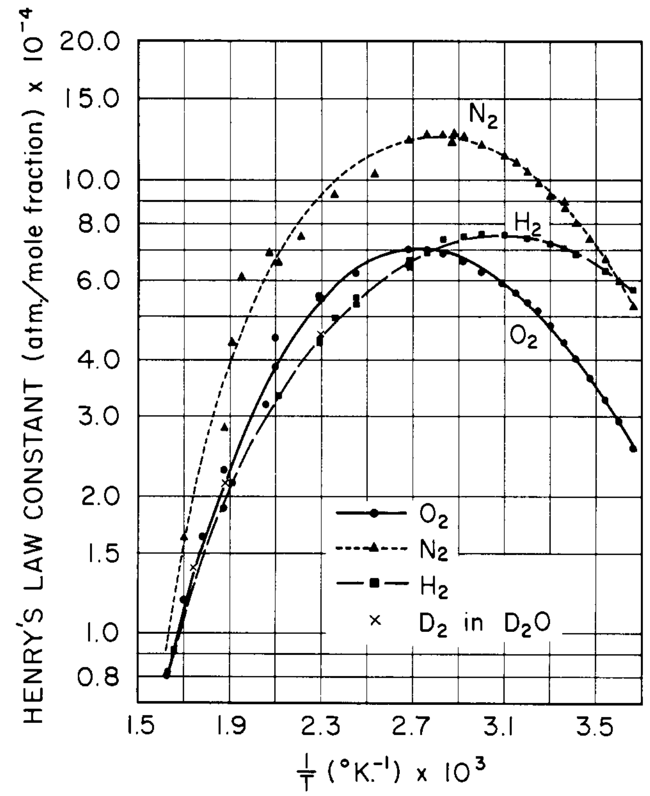

Figure 1. Solubility of oxygen, nitrogen, and hydrogen in water

Values for the solubility of deterium in deuterium oxide (heavy water) and also of xenon in deuterium oxide (*23*) corrected as follows for the density difference:

$$\text{Soly. Xe in } H_2O = \text{soly. Xe in } D_2O \left(\frac{\text{density } D_2O}{\text{density } H_2O}\right) \tag{7}$$

$$= \text{soly. Xe in } D_2O\ (1.11) \tag{7a}$$

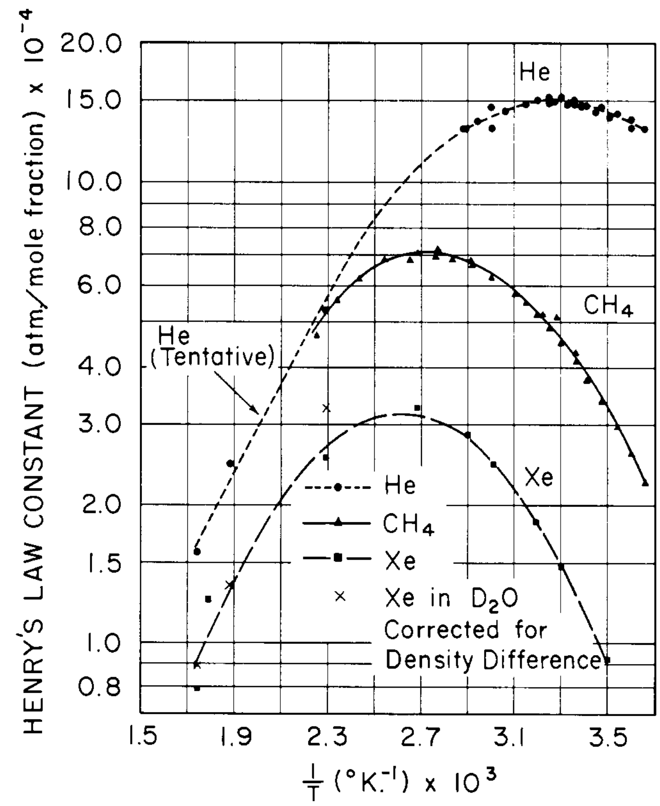

Figure 2. Solubility of helium, xenon, and methane in water

are included in Figures 1 and 2 for comparative purposes.

An examination of Figures 1 and 2 showed that a parabolic fit would be effective for all curves; however, it appeared as if the axes for the curves, such as the one for oxygen, were not parallel to the H and $1/T$ coordinates, but were rotated by some small angle (5° in the case of oxygen). This rotation required that the curves be fit by a general equation of the second degree in the form

$$A(\log \bar{H})^2 + B(1/\bar{T})^2 + C(\log \bar{H})(1/\bar{T}) + D(\log \bar{H}) + E(1/\bar{T}) - 1 = 0 \qquad (8)$$

rather than of the simpler form (see footnote, Table II)

$$\log(H) = a + b\left(\frac{1}{T}\right) + c\left(\frac{1}{T}\right)^2 \qquad (9)$$

The best fitting constants for Equation 8 were determined by an iterative least square technique on a IBM 650 computer and are tabulated with the maximum and average percentage deviation of the experimental values of H from the predicted values for each gas (Table II). The equations of best fit are shown in Figures 1 and 2. The data for oxygen and nitrogen include two or three points which deviate widely from the predicted values of H. Because the average deviation is so low, including these points in the calculation of deviation, it is believed that they probably represent the effect of experimental uncertainties. Inasmuch as the assembly of data represents a larger number of individual experimenters in the case of oxygen and nitrogen than the other gases it is not too surprising to find a greater degree of erratic variation among their collective results.

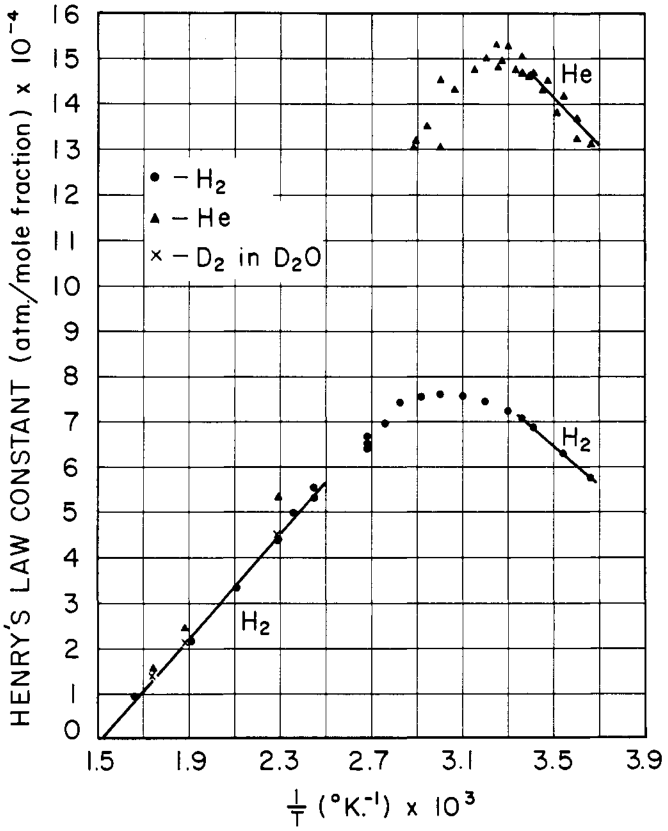

Figure 3. Solubility of hydrogen and helium in water

For convenience in calculation to give smaller numbers, the constants in Table II which fit Equation 8 are valid only if $\bar{H}$ in Equation 8 is expressed as $H \times 10^{-4}$ and $(1/\bar{T})$ is expressed as $(1/T) \times 10^3$.

After numerical values for one variable have been introduced into Equation 8, a quadratic equation in the other variable results. It is recommended that a graphical method of obtaining the solution of this quadratic equation be employed after $\bar{H}$ or $(1/\bar{T})$ have been substituted in it. Use of the usual solution for a quadratic equation will frequently be frustrating, because differences in large approximately equal numbers must be secured, and this may introduce a large error in the expected result.

Since the resulting equation of correlation, Equation 8, proved to be somewhat complex, a second type of correlation for the same solubility data was carried out. As evident in Figures 3 to 5 for the values of H plotted *vs.* $1/T$, in both the low and high temperature range H is a linear function of $1/T$, so that both sides of the Henry's law curve in Figures 3 to 5 could be correlated as follows:

$$H = a + b\left(\frac{1}{T}\right) \qquad (10a)$$

$$H = a' + b'\left(\frac{1}{T}\right) \qquad (10b)$$

where

a, b = correlation constants for the high temperature range

a', b' = correlation constants for the low temperature range

The least square values of a, b, a', and b' are listed in Table III with the average deviation, maximum deviation, and applicable temperature range. Only four points are available for methane, so the reliability of the constants in Table III for this gas is not too high. One point for nitrogen and two points for oxygen near the horizontal axis showed small absolute error but high percentage error, and have been omitted in the calculation of a and b. In the low temperature range for helium both the data of Morrison and Johnstone (*12*) and Seidell (*19-21*) [or Lawrence (*9*)] were used, although there appears to be some conflict among the reported results. For xenon in this range only the data of Morrison and Johnstone were used. If information is required about solubilities within the indicated temperature ranges, Equations 10a or 10b provide a satisfactory and simple method of obtaining the desired values.

Table II. Constants for the General Solubility Correlation Equation

	Correlation Constants for Equation 8					Deviation ($H_{calcd.} - H_{exptl.}$)	
Gas	A	B	C	D	E	Max. %	Av. %
O_2	−0.0005943	−0.1470	−0.05120	−0.1076	0.8447	14.3	2.8
N_2	−0.1021	−0.1482	−0.01900	−0.03741	0.8510	30.6	4.3
H_2	−0.1233	−0.1366	0.02155	−0.2368	0.8249	3.4	1.3
He	0.1216	−0.1146	−0.06702	−0.3277	0.8257	7.0	1.9
Xe	0.0001156	−0.1632	−0.003025	−0.2264	0.8541	16.0	5.3
CH_4	−0.1173	−0.1247	−0.07629	0.1959	0.7413	7.8	1.4

In using these values in Equation 8, $\bar{H} = H \times 10^{-4}$ and $(1/\bar{T}) = (1/T) \times 10^3$.

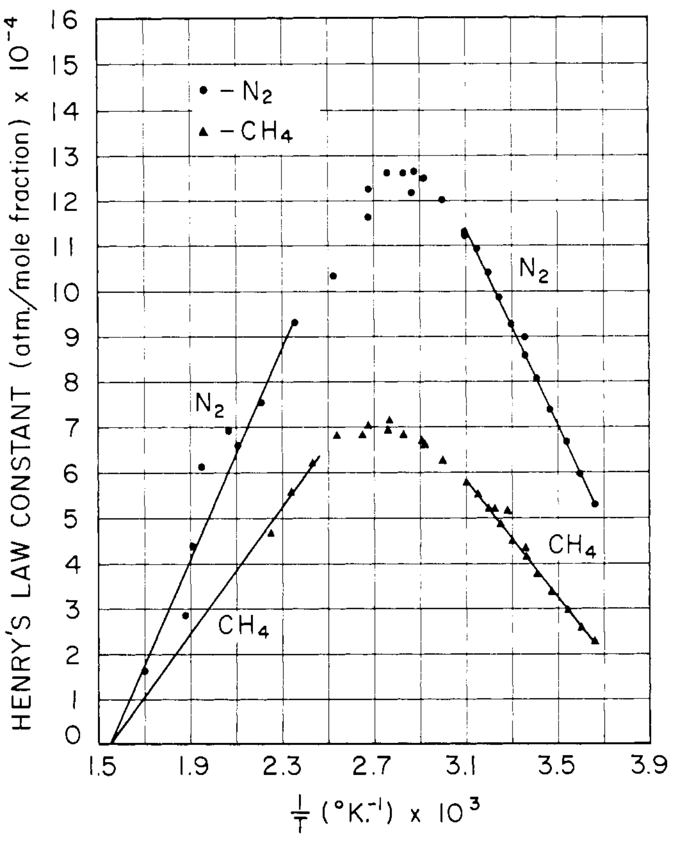

Figure 4. Solubility of nitrogen and methane in water

If the maximum value of H, and $1/T$ at this value, can be determined, two new functions can be defined:

$$H^* = H/H_{\max} \quad (11)$$

where $H_{\max}$ = maximum value of the H vs. $1/T$ curve

and

$$\left(\frac{1}{T}\right)^* = \frac{\left(\frac{1}{T}\right) - \left(\frac{1}{T_c}\right)}{\left(\frac{1}{T_{\max}}\right) - \left(\frac{1}{T_c}\right)} \quad (12)$$

where

T_c = critical temperature of water = 647° K.

$(1/T_{\max})$ = value of $1/T$ at $H_{\max}$

It is then possible to plot log H^* vs. $(1/T)^*$ for oxygen, nitrogen, hydrogen, helium, xenon, and methane as shown in Figure 6. The values of $H_{\max}$ and $(1/T_{\max})$ listed in Table IV were obtained by finding the maximum value of H from Equation 8 and the corresponding $(1/T_{\max})$. The points in Figure 6 are correlated relatively well by the following equation as determined by a least square technique:

$$\log H^* = 1.142 - 2.846 \left(\frac{1}{T}\right)^* + 2.486 \left(\frac{1}{T}\right)^{*2} - 0.9761 \left(\frac{1}{T}\right)^{*3} + 0.2001 \left(\frac{1}{T}\right)^{*4} \quad (13)$$

With the exception of xenon the error in Equation 13 is less than 3% for the range from 10° to 160° C. The deviation at the temperature extremes from this equation is shown in Table IV.

RELATIVE VOLATILITY

In the ideal solution where Equation 2 applies, it is often convenient to use relative volatility relations in systems where more than one gas is dissolved in water. If the normal definition of relative volatility is adopted, then

Table III. Constants for the Discontinuous Linear Solubility Correlation Equations

Gas	Temp. Range, °C.	$a \times 10^{-4}$	% Dev.[a]	$b \times 10^{-7}$	% Dev.[a]	% Dev. of Predicted H[b]	
						Max.	Av.
			High Temperature Range				
O_2	153-374	−10.94	± 7.7	7.09	± 8.3	20.0	7.9
N_2	151-374	−17.65	±21.5	11.41	±22.8	39.4	12.3
H_2	120-374	− 9.01	± 5.8	5.83	± 5.2	4.2	1.6
He			Insufficient data				
Xe			Insufficient data				
CH_4	139-374	−10.69	±33.0	6.91	±46.5	12.2	5.1
			Low Temperature Range				
O_2	0-51	24.49	±2.5	− 5.99	±3.1	2.8	1.6
N_2	0-50	45.32	±4.8	−10.92	±5.2	4.2	2.3
H_2	0-25	21.13	±2.8	− 4.20	±3.5	0.8	0.6
He	0-22	30.56	±5.4	− 4.72	±5.6	4.8	1.7
Xe	0-72	12.35	±7.3	3.28	±8.6	6.5	2.4
CH_4	0-50	25.76	±7.6	− 6.43	±7.2	8.9	2.5

[a] For 95% confidence limits.
[b] Calculated H minus experimental H divided by calculated value.

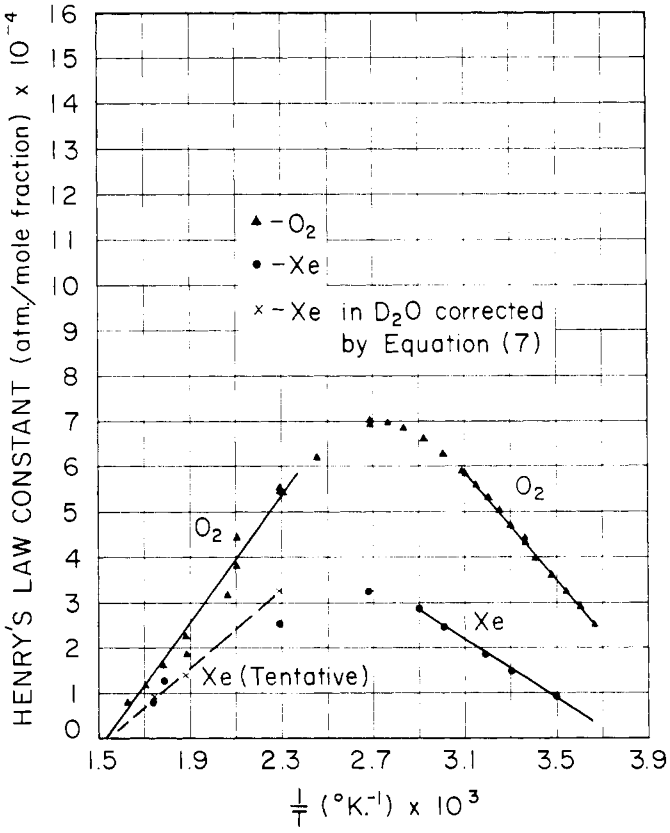

Figure 5. Solubility of oxygen and xenon in water

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (14)$$

where

α_{12} = relative volatility of gaseous component 1 with respect to component 2

y = mole fraction in the vapor phase of any component

x = mole fraction in the liquid phase of any component

Henry's law applies to systems with an ideal gas phase;

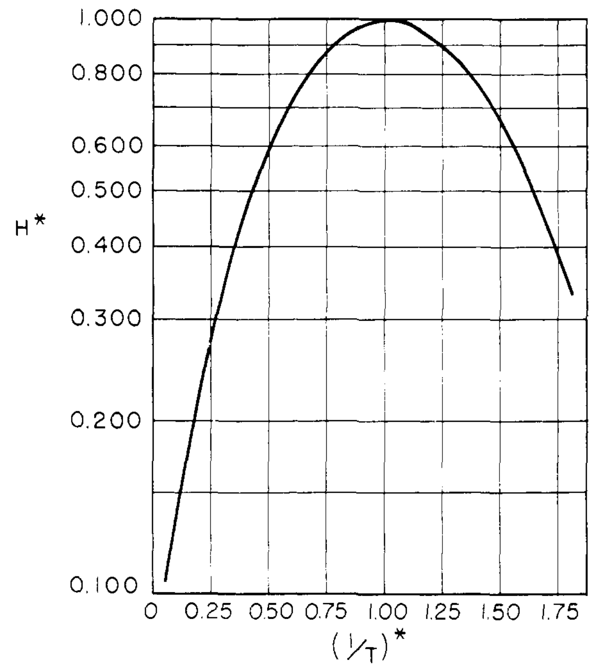

Figure 6. Generalized solubility correlation

therefore, if the relationship between the liquid and gas phase as shown by Equation 2 is:

$$Py = p = H(x) \qquad (2a)$$

where P = total pressure of the system, then α_{12} is merely

$$\alpha_{12} = H_1/H_2 \qquad (15)$$

This expression is useful in evaluating the relative concentration of one or more gases in the vapor phase above an aqueous solution. Using hydrogen as the reference gas, relative volatility values based on Equations 8 and 15 have been plotted *vs.* temperature in ° C. in Figure 7.

EFFECT OF PRESSURE ON THE HENRY'S LAW CONSTANT

The values of the Henry's law constants discussed so far are for ideal liquid and vapor phase solutions, and apply in practical cases to low pressures only. "Low pressures" in the case of oxygen appear to be 1500 p.s.i.a. at 100° C. (212° F.) to about 2000 p.s.i.a. at 300° C. (572° F.). For the other gases considered here, the "low pressures" ranges in which Henry's law appears applicable are shown in Table V.

A general discussion of the effect of pressure on the solubility of gases (including multiphase formation) may be found in references (*6, 7, 10, 22*). For engineering purposes, if information is desired for higher pressures than those listed in Table V, it is best to refer to the original experimental data, or use the technique of Krichevsky and Kasarnovsky (*6*) if no data are available at the desired conditions. It is impossible to compute the solubility of a gas in water at very high pressures by multiplying the gas partial pressure by a fugacity correction and introducing this computed fugacity in Equation 1. The solubility computed in this manner is usually further from the experimental solubility than if no correction had been applied at all. For example, the solubility of hydrogen at 100° C. and 1000 atm. computed using the generalized fugacity charts of Hougen and Watson is found to be 28.7 cc. of gas at standard temperature and pressure per gram of water, while the experimental solubulity is 15.8 cc. of gas at standard temperature and pressure per gram of water. By using Krichevsky and Kasarnovsky's technique for the same set of conditions, the predicted solubility is 15.5 cc. of gas at standard temperature and pressure per gram of water.

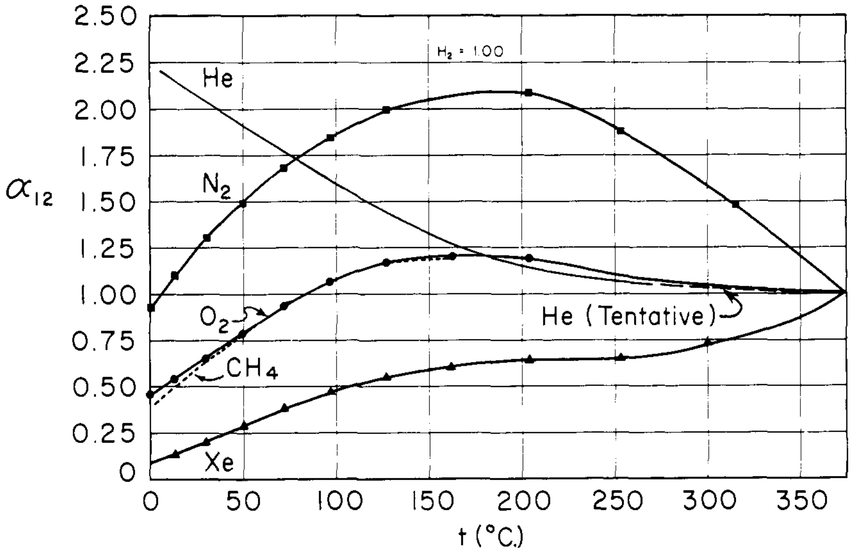

Figure 7. Relative volatility of ideal gases in water

Table IV. Data for Generalized Solubility Correlation

	Gas					
	O_2	N_2	H_2	He	Xe	CH_4
$H_{max} \times 10^{-4}$	7.08	12.39	7.54	14.99	3.17	7.02
$(1/T_{max}) \times 10^3$	2.73	2.80	3.09	3.26	2.61	2.71
% error of Equation 13 at extreme of low temperature range	9.9	6.0	4.5	3.8	3.4	0.3
% error of Equation 13 at extreme of high temperature range	7.3	15.1	5.2	23.8	42.6	7.8

Table V. Approximate Maximum Pressure to Which Henry's Law Can Be Applied

Temp.		Gas Partial Pressure, P.S.I.A.					
° C.	° F.	O_2	N_2	H_2	He	Xe	CH_4
0	32	1500	750	1500	1500	300[a]	400
100	212	1500	750	1500	1500	300[a]	500
300	572	2000	750[a]	2000	300[a]	300[a]	..[b]

[a] Maximum range of available data—proable pressure is higher.

[b] No data available.

SOLUBILITY OF MIXTURES OF GASES

In the range of pressure in which Henry's law holds, Weibe and Gaddy (*25*) for hydrogen-nitrogen mixtures and Smith and Katz (*22*) for hydrogen-oxygen and nitrogen-oxygen mixtures have shown that each gaseous component acts independently of the other. Thus, once the solubility of each component has been obtained, the solubility of a mixture of gases can be determined by multiplying each component by its vapor phase mole fraction, and summing these weighted solubilities together. For example, in a nitrogen-hydrogen mixture using experimental solubilities,

$$(S_{N_2})(y_{N_2}) + (S_{H_2})(y_{H_2}) = S_{\text{mixture}} \qquad (16)$$

where

S = solubility in the liquid phase, cc. of gas at S.T.P. per gram of water

y = mole fraction in gas phase.

The error in this technique is reported to be 1.5% at 100 atm. and 3% at 1000 atm. (*25*). The mole fraction in the liquid phase is not used as the weighting factor for the solubility of the components. If Henry's law constants calculated from Equation 8 or Equation 10 rather than experimental values are to be used, and the total pressure and mole fraction of each component in the gas phase are known, it is necessary to first compute the solubility in the liquid phase of each component by Equation 2. For example, at 25° C. and 100 atm. for a mixture of 76.4% hydrogen and 23.6% nitrogen, assuming no pressure corrections are required,

$$P_{H_2} + P_{N_2} + P_{H_2O} = P_T$$

$$P_{H_2O} \ll P_{H_2} \text{ and } P_{H_2O} \ll P_{N_2} \text{ so } P_{H_2} + P_{N_2} = P_T$$

At 25° C. from Equation 8

$$H_{H_2} = 7.09 \times 10^4$$

$$H_{N_2} = 8.78 \times 10^4$$

$$\text{Solubility} \frac{\text{cc. at S.T.P.}}{\text{g. } H_2O} = 1244 \frac{P_i}{H_i} = 1244 \frac{P_T y_i}{H_i} \text{ if } P_i \text{ is in atm.}$$

and H is atm. per mole fraction

$$\text{Soly.}_{H_2} = \frac{1244(100)(0.764)}{7.09 \times 10^4} = 1.34$$

$$\text{Soly.}_{N_2} = \frac{1244(100)(0.236)}{8.78 \times 10^4} = 0.33$$

$$\text{Soly.}_{\text{mixture}} = \text{Soly.}_{H_2} + \text{Soly.}_{N_2} = 1.67 \ \frac{\text{cc. at S.T.P.}}{\text{g. } H_2O}$$

The experimental value as given by Wiebe and Gaddy (*25*) for these conditions is 1.64 cc. at standard temperature and pressure per gram of water.

To obtain greater accuracy if the vapor pressure of water is more substantial, Smith and Katz (*22*) suggest using the total pressure minus the vapor pressure of water ($P_T - p_{H_2O}$) as the pressure to be substututed in lieu of P_T in the equation

$$p_i = P_T y_i.$$

SOLUBILITY IN AQUEOUS SALT SOLUTIONS

The solubility of gases as affected by the presence of other solutes is covered in this discussion because the topic is complex and has been considered elsewhere (*10, 16, 17, 23*).

LITERATURE CITED

(1) Culbertson, O. L., McKetta, J. J., Jr., *J. Petrol. Technol.* **3**, 223 (1951).

(2) Friend, Leo, Adler, S. B., *Chem. Eng. Progr.* **53**, 452 (1957).

(3) Glew, D. N., Moelwyn-Hughes, E. A., *Discussions Faraday Soc.* **1953**, No. 15, 150.

(4) Goodman, J. B., Krase, N. W., *Ind. Eng. Chem.* **23**, 401 (1931).

(5) Henry, William, *Phil. Trans.* **93**, 29,274 (1803).

(6) Krichevsky, I. R., Kasarnovsky, J. S., *J. Am. Chem. Soc.* **57**, 2168 (1935).

(7) Lachowicz, S. K., *J. Imp. Coll. Chem. Eng. Soc.* **8**, 51 (1954).

(8) Lange, N. A., "Handbook of Chemistry," 9th ed., Handbook Publ., Sandusky, Ohio, 1956.

(9) Lawrence, J. H., Loomis, W. F., Tobias, C. A., Turpin, F. H., *J. Physiol.* **105**, 197 (1946).

(10) Markham, A. E., Kobe, K. A., *Chem. Revs.* **28**, 521 (1941).

(11) Michels, A., Grever, J., Bijl, A., *Physica* **3**, 797 (1936).

(12) Morrison, T. J., Johnstone, N. B., *J. Chem. Soc.* **1954**, 3441.

(13) Perry, J. H., "Chemical Engineers' Handbook," 3rd ed., McGraw-Hill, New York, 1950.

(14) Pray, H. A., Schweickert, C. E., Minnich, B. H. *Ind. Eng. Chem.* **44**, 1146 (1952); Battelle Memorial Inst., Columbus 1, Ohio, **BMI-T-25**, May 15, 1950.

(15) Pray, H. A., Stephan, E. F., "Solubility of Hydrogen in Uranyl Sulphate Solutions at Elevated Temperatures," *Ibid.*, **BMI-840**, June 10, 1953.

(16) Pray, H. A., Stephan, E. F., "Solubility of Hydrogen in Uranyl Sulphate Solutions at Elevated Temperatures," *Ibid.*, **BMI-870**, Sept. 25, 1953.

(17) Pray, H. A., Stephan, E. F., "Solubility of Hydrogen and Oxygen in Uranyl Fluoride Solutions at Elevated Temperatures," *Ibid.*, **BMI-897**, Jan. 18, 1954.

(18) Saddington, A. W., Krase, N. W., *J. Am. Chem. Soc.* **56**, 353 (1934).

(19) Seidell, Atherton, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., vol. **I**, Van Nostrand, New York, 1940.

(20) Seidell, Atherton, "Solubilities of Organic Compounds," 3rd ed., vol. **2**, Van Nostrand, New York, 1941.

(21) Seidell, Atherton, Linke, W. F., "Solubilities of Inorganic and Organic Compounds," Suppl. to 3rd ed., Van Nostrand, New York, 1952.

(22) Smith, M. J., Katz, D. L., "Physical Behavior of the H_2-O_2-H_2O System under Pressure," Oak Ridge Natl. Lab., Oak Ridge, Tenn., **ORNL-1069**, (Sept. 24, 1951).

(23) Stephan, E. F., Hatfield, N. S., Peoples, R. S., Pray, H. A., "Solubility of Gases in Water and in Aqueous Uranyl Salt Solutions at Elevated Temperatures and Pressures,"Battelle Memorial Inst., Columbus 1, Ohio **BMI-1067**, Jan. 23, 1956.

(24) Suciu, S. N., Sibbitt, W. L., "A Study of Nitrogen and Water and Hydrogen and Water Systems at Elevated Temperatures Pressures," Argonne Natl. Lab., Lemont, Ill., **ANL-4603**, Pt. II, 1951.

(25) Wiebe, R., Gaddy, V. L., *J. Am. Chem. Soc.* **56**, 76 (1934); **57**, 1487 (1935).

(26) *Ibid.*, **57**, 847 (1935).

(27) Wiebe, R., Gaddy, V. L., Heins, Conrad, Jr., *Ibid.*, **55**, 947 (1933).

(28) Winkler, L. W., *Ber.* **34**, 1408 (1901).

(29) Zoss, L. M., Suciu, S. N., Sibbitt, W. L., *Trans. Am. Soc. Mech. Engrs.* **76**, 69 (1954).

RECEIVED for review October 6, 1958. Accepted April 9, 1959.