

# Henry's Constants and Vapor-Liquid Distribution Constants for Gaseous Solutes in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ at High Temperatures

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# Henry's Constants and Vapor–Liquid Distribution Constants for Gaseous Solutes in H<sub>2</sub>O and D<sub>2</sub>O at High Temperatures

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We have developed correlations for the Henry's constant  $k_H$  and the vapor–liquid distribution constant  $K_D$  for 14 solutes in H<sub>2</sub>O and seven solutes in D<sub>2</sub>O. The solutes considered are common gases that might be encountered in geochemistry or the power industry. Solubility data from the literature were critically assessed and reduced to the appropriate thermodynamic quantities, making use of corrections for nonideality in the vapor and liquid phases as best they could be computed. While the correlations presented here cover the entire range of temperatures from near the freezing point of the solvent to high temperatures approaching its critical point, the main emphasis is on representation of the high-temperature behavior, making use of asymptotic relationships that constrain the temperature dependence of  $k_H$  and  $K_D$  near the critical point of the solvent. © 2003 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [DOI: 10.1063/1.1564818]

Key words: distribution constant; gases; heavy water; Henry's constant; solubility; vapor–liquid equilibrium; water.

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## 1. Introduction

The solubilities of gases in water, and their distribution between coexisting vapor and liquid phases, are important in a variety of contexts. Aqueous gas solubilities are needed for design calculations in chemical processing and for many geochemical studies. In steam power plants, the distribution of solutes between water and steam is important. In hydrothermal systems, corrosion often depends on the concentration of solutes. For many gases, accurate measurements of solubility exist at temperatures near 25 °C, but data at higher temperatures are much more sparse and scattered. Since many of the important applications are at high temperatures, there is a need for evaluated data and careful correlation to provide scientists and engineers with the best possible data at high-temperature conditions.

The fundamental thermodynamic quantity describing the solubility of a gas in a liquid is the Henry's constant  $k_H$ , defined by

$$k_H = \lim_{x_2 \rightarrow 0} (f_2/x_2), \quad (1)$$

where  $f_2$  and  $x_2$  are, respectively, the liquid-phase fugacity and mole fraction of the solute. While this definition can be applied at any state of the solvent, in this work we restrict our attention to vapor-liquid equilibrium conditions in single solvents, so that  $k_H$  is a function only of temperature along the saturation curve of the solvent. A related quantity is the vapor-liquid distribution constant  $K_D$ , defined by

$$K_D = \lim_{x_2 \rightarrow 0} (y_2/x_2), \quad (2)$$

where  $y_2$  is the vapor-phase solute mole fraction in equilibrium with the liquid.

Fernández-Prini and Crovetto (1989) examined solubility data as a function of temperature for ten nonpolar gases in ordinary water (which we will call  $H_2O$ , despite the fact that it is not isotopically pure) and seven in heavy water ( $D_2O$ ). They converted the data to Henry's constants and fitted them

to a polynomial. The correlations from that work were adopted as a Guideline by IAPWS, the International Association for the Properties of Water and Steam (IAPWS, 1995a). Several factors suggest the need for a revision at this time.

First, more is understood about the behavior of  $k_H$  at high temperatures, particularly in the neighborhood of the critical point of the solvent. Japas and Levelt Sengers (1989) derived linear relationships, valid in the vicinity of the solvent critical point, relating both  $k_H$  and  $K_D$  to the solvent density. The relationship for  $k_H$  was exploited (Harvey and Levelt Sengers, 1990; Harvey, 1996) to produce correlations that were better able to fit Henry's constant data at high temperatures and that had superior extrapolation behavior. Revised formulations should take advantage of this advance rather than relying on polynomials with little physical basis.

Second, better methods are available for reducing high-temperature solubility data to Henry's constants. These methods, some of which have been presented previously (Fernández-Prini *et al.*, 1992; Alvarez *et al.*, 1994), will be discussed in a subsequent section.

Third, additional data exist for some aqueous systems, including a few systems not included in the original work of Fernández-Prini and Crovetto (1989). We are now able to produce correlations for four additional solutes in  $H_2O$ .

Fourth, new standards have been adopted for the representation of both the thermodynamic temperature scale (Preston-Thomas, 1990) and the thermodynamic properties of pure water (IAPWS, 2000a; Wagner and Pruß, 2002). While neither of these changes is likely to make a significant difference within the uncertainty to which high-temperature Henry's constants are known, it is still desirable to be consistent with the latest standards.

Finally, we mention that correlations for  $K_D$  for ten solutes in  $H_2O$  were produced by Alvarez *et al.* (1994) and later adopted as an IAPWS Guideline (IAPWS, 2000b). This work did take advantage of the theoretical advance of Japas and Levelt Sengers (1989), and is therefore less in need of revision. However, we revise it here in order to add more solutes and reevaluate some data for the old solutes, and to produce correlations for  $k_H$  and  $K_D$  that are based on the same data.

The purpose of this work is to provide reliable values for  $k_H$  and  $K_D$  for applications at high temperatures. The highly precise  $k_H$  data available for many aqueous solutes between approximately 0 and 60 °C are not described to within their uncertainty by the correlations presented in this work. Those whose interest is confined to this temperature range should not use our correlations; instead they should use the smoothing equations for  $k_H$  in the papers (referenced in the next section) where these high-quality measurements are reported.

## 2. Data Sources

For many solutes, there have been numerous studies, of widely varying quality, of their solubility in water near 25 °C. In the past 30 years, techniques have been developed (Battino, 1989) for highly accurate measurement of solubili-

ties of gases in water at low temperature and near-atmospheric pressure, rendering most earlier work obsolete. In systems where such high-quality studies have been performed, we relied exclusively on those data over the temperature range they covered. For the few systems considered where such studies do not exist, we chose one or more studies of solubility versus temperature that we believed to be most reliable, in some cases relying on existing critical evaluations (Battino and Wilhelm, 1981; Carroll and Mather, 1989; Crovetto, 1991; Carroll *et al.*, 1991).

At higher temperatures, we began with the bibliography collected by Fernández-Prini and Crovetto (1989). This was supplemented by literature searches for data that were too recent to be included in that work, and for data on additional solutes. In many cases, studies with high-temperature data also contained measurements at lower temperatures covered by the previously mentioned high-precision data. In these cases, we included their low-temperature points in the data to be fit, although in many cases they were ultimately discarded as outliers in the fitting process.

The high-precision data at low temperatures were obtained with solute partial pressures  $p_2$  that generally did not exceed atmospheric pressure. At high temperatures, the values of  $p_2$  are usually larger. We refer to these two experimental techniques as the low-temperature and the high-temperature methods, respectively. It should be noted that some studies have employed the "high-temperature" method also at low temperatures.

Reported temperatures were converted to the ITS-90 temperature scale by standard procedures. Often, the temperature scale used for the measurements was not reported, so it was inferred by the date of the publication. Temperature-scale differences are only non-negligible compared to experimental uncertainties for the high-precision, low-temperature data, but all data were converted to ITS-90 for the sake of consistency.

Table 1 shows all the data sources used in this study for solutes in H<sub>2</sub>O. The preferred low-temperature sources are listed first for each solute; other sources are then listed in chronological order. Table 2 contains the same information for solutes in D<sub>2</sub>O. We are not aware of any solubility studies for gases in tritium oxide (T<sub>2</sub>O), but we did not make a thorough search for such data.

### 3. Conversion of Data to $k_H$ and $K_D$

#### 3.1. Thermodynamic Relations

In order to determine  $k_H$  or  $K_D$  as defined by Eqs. (1) and (2) from gas solubility data, a thorough thermodynamic description of the binary gas-liquid equilibrium is needed. This level of description is necessary when the goal is to cover the complete range of existence of the liquid solvent, from its triple-point temperature  $T_t$  to its critical temperature  $T_{c1}$ . Close to  $T_t$ , the gas phase consists mainly of the gaseous solute, while close to  $T_{c1}$  the two fluid phases become progressively similar in density and composition. At higher temperatures, the solvent often predominates in the gas phase

due to its high vapor pressure; this is especially true of aqueous systems because the critical pressure  $p_{c1}$  is much larger for water (and D<sub>2</sub>O) than for most other liquids. Finally, at  $T_{c1}$ , the gas and liquid phases become identical and  $K_D = 1$ . The calculation of  $k_H$  at lower temperatures is much simpler, because many simplifying assumptions can be made based on the large difference between the properties of the vapor and the liquid phases; this is not possible at higher temperatures where the vapor pressure of the solvent is large.

The starting point for the thermodynamic analysis is the equality of chemical potentials of each component in the coexisting phases. For the solvent, this produces (Fernández-Prini and Crovetto, 1989)

$$\begin{aligned}\mu_1(\text{g}; T, p, y_1) &= \mu_1^\oplus(T) + RT \ln \frac{f_1}{p^\oplus} \\ &= \mu_1^*(T) + RT \ln a_1^R + \int_{p_1^*}^p V_1^* dp \\ &= \mu_1(1; T, p, x_1),\end{aligned}\quad (3)$$

where  $\mu_1^\oplus(T)$  and  $\mu_1^*(T)$  are the standard chemical potentials of the solvent in the vapor and in the pure liquid, respectively,  $R$  is the molar gas constant, and  $p^\oplus = 0.1$  MPa is the standard-state pressure;  $f_1$  is the fugacity of the solvent in the vapor, and  $a_1^R$  is its activity in the liquid using the Raoult activity scale; and  $p_1^*$  is the vapor pressure and  $V_1^*$  the molar volume of the pure solvent. Because the gaseous solutes that we consider in this work are only slightly soluble in water, it may be assumed for all practical purposes that  $a_1^R \cong 1$ , so that Eq. (3) becomes

$$\ln \frac{y_1 \phi_1 p}{\phi_1^* p_1^*} = \int_{p_1^*}^p \frac{V_1^*}{RT} dp, \quad (4)$$

where  $\phi_1$  is the fugacity coefficient of the solvent in the coexisting vapor and  $\phi_1^*$  is the fugacity coefficient of the pure solvent at saturation.

For the solute, the condition of equilibrium between the two coexisting phases, using Henry's (unsymmetric) activity scale for the liquid phase, is

$$\begin{aligned}\mu_2(\text{g}; T, p, y_2) &= \mu_2^\oplus(T) + RT \ln \frac{f_2}{p^\oplus} \\ &= \mu_2^\infty(T) + RT \ln a_2^H + \int_{p_1^*}^p V_2^\infty dp \\ &= \mu_2(1; T, p, x_2),\end{aligned}\quad (5)$$

where  $\mu_2^\infty$  and  $V_2^\infty$  are the chemical potential and partial molar volume of the solute in its standard state of infinite dilution, and  $a_2^H$  is the activity of the solute in the solution according to the unsymmetric Henry scale (O'Connell, 1977). The activity of the solute can be expressed as the product of an ideal factor ( $x_2$ ) and a nonideal factor (activity coefficient  $\gamma_2^H$ ), so that  $a_2^H = x_2 \gamma_2^H$ . From the relation between the standard states for gases and for solutes at infinite dilution (Fernández-Prini *et al.*, 1992) contained in Eq. (5), we get

TABLE 1. Data sources for gas solubility in H<sub>2</sub>O

Solute	Reference	No. of points (accepted)	$T_{\min}/\text{K}$	$T_{\max}/\text{K}$
He	Krause and Benson (1989)	32(32)	273.21	333.13
	Wiebe and Gaddy (1935)	2(2)	323.13	348.12
	Pray <i>et al.</i> (1952)	3(0)	435.89	588.74
	Stephen <i>et al.</i> (1962)	3(3)	473.15	553.18
	Gardiner and Smith (1972)	2(0)	323.13	373.12
	Potter and Clynne (1978)	4(3)	377.12	548.21
Ne	Krause and Benson (1989)	34(34)	273.20	333.14
	Potter and Clynne (1978)	5(2)	343.18	556.86
	Crovetto <i>et al.</i> (1982)	7(7)	294.89	543.36
Ar	Krause and Benson (1989)	60(60)	273.19	333.14
	Rettich <i>et al.</i> (1992)	22(22)	275.10	313.14
	Potter and Clynne (1978)	15(5)	298.20	561.08
Kr	Crovetto <i>et al.</i> (1982)	8(8)	306.89	568.36
	Krause and Benson (1989)	36(36)	273.19	333.14
	Potter and Clynne (1978)	4(3)	343.33	525.56
Xe	Crovetto <i>et al.</i> (1982)	6(6)	333.68	523.36
	Krause and Benson (1989)	30(30)	273.22	333.14
	Stephen <i>et al.</i> (1956)	4(4)	373.12	574.85
H <sub>2</sub>	Potter and Clynne (1978)	5(1)	343.38	557.31
	Crovetto <i>et al.</i> (1982)	6(5)	334.48	476.26
	Battino and Wilhelm (1981)	17(17)	273.15	353.13
	Wiebe and Gaddy (1934)	3(3)	323.13	373.12
	Ipatieff and Teveloromush (1934)	6(3)	373.12	498.16
	Pray <i>et al.</i> (1952)	4(2)	324.80	616.52
N <sub>2</sub>	Stephen <i>et al.</i> (1956)	3(0)	373.12	435.92
	Alvarez and Fernández-Prini (1991)	26(26)	318.89	636.09
	Morris <i>et al.</i> (2001)	45(34)	460.50	581.30
	Rettich <i>et al.</i> (1984)	17(17)	278.12	323.14
	Goodman and Krase (1931)	4(2)	353.12	442.14
	Wiebe <i>et al.</i> (1933)	3(3)	323.13	373.12
O <sub>2</sub>	Saddington and Krase (1934)	15(11)	323.13	513.17
	Pray <i>et al.</i> (1952)	2(1)	533.17	588.75
	O'Sullivan and Smith (1970)	3(2)	324.63	398.13
	Alvarez and Fernández-Prini (1991)	31(31)	336.28	636.46
	Rettich <i>et al.</i> (2000)	32(32)	274.15	328.13
	Stephen <i>et al.</i> (1956)	8(7)	373.12	616.52
CO	Cramer (1982)	15(13)	322.74	561.11
	Rettich <i>et al.</i> (1982)	14(14)	278.15	323.09
	Gillespie and Wilson (1980)	5(3)	310.92	588.67
CO <sub>2</sub>	Morrison and Billet (1952)	19(19)	286.44	347.82
	Murray and Riley (1971)	8(8)	274.19	308.14
	Wiebe and Gaddy (1939)	3(3)	323.13	373.12
	Wiebe and Gaddy (1940)	6(3)	285.14	313.13
	Malinin (1959)	4(4)	473.15	603.19
	Ellis and Golding (1963)	11(9)	450.14	607.19
	Takenouchi and Kennedy (1964)	10(9)	383.13	623.19
	Zawisza and Malesinska (1981)	7(7)	323.14	473.11
	Cramer (1982)	7(3)	306.14	486.21
	Shagiakhmetov and Tarzimanov (1982)	3(2)	323.14	423.11
H <sub>2</sub> S	Müller <i>et al.</i> (1988)	6(6)	373.12	473.11
	Nighswander <i>et al.</i> (1989)	4(2)	353.58	471.06
	Crovetto and Wood (1992)	3(3)	622.96	642.66
	Bamberger <i>et al.</i> (2000)	3(2)	323.20	353.10
	Carroll and Mather (1989)	10(10)	273.15	333.13
	Selleck <i>et al.</i> (1952)	5(3)	310.91	444.25
CH <sub>4</sub>	Lee and Mather (1977)	11(11)	283.10	453.06
	Gillespie and Wilson (1982)	6(3)	310.92	588.60
	Rettich <i>et al.</i> (1981)	16(16)	275.46	328.14
	Michels <i>et al.</i> (1936)	5(4)	323.13	423.14
	Culberson and McKetta (1951)	9(6)	298.14	466.45
	Sultanov <i>et al.</i> (1972)	7(5)	423.11	633.11
C <sub>2</sub> H <sub>6</sub>	Cramer (1982)	10(7)	334.13	573.11
	Crovetto <i>et al.</i> (1982)	7(7)	297.49	518.26
	Rettich <i>et al.</i> (1981)	23(23)	275.44	323.14
	Culberson and McKetta (1950)	5(2)	310.91	444.25
SF <sub>6</sub>	Crovetto <i>et al.</i> (1984)	22(22)	295.39	473.46
	Ashton <i>et al.</i> (1968)	15(13)	283.14	323.13
	Park <i>et al.</i> (1982)	1(1)	298.14	298.14
	Mroczek (1997)	33(32)	347.25	505.55

TABLE 2. Data sources for gas solubility in D<sub>2</sub>O

Solute	Reference	No. of points (accepted)	$T_{\min}/\text{K}$	$T_{\max}/\text{K}$
He	Scharlin and Battino (1992)	7(7)	288.15	318.19
	Stephen <i>et al.</i> (1962)	6(5)	323.13	553.18
Ne	Scharlin and Battino (1992)	6(6)	288.18	318.20
	Crovetto <i>et al.</i> (1982)	9(9)	293.20	549.96
Ar	Scharlin and Battino (1992)	4(4)	288.30	318.14
	Crovetto <i>et al.</i> (1982)	14(13)	296.59	583.76
Kr	Scharlin and Battino (1992)	4(4)	288.19	318.14
	Crovetto <i>et al.</i> (1982)	6(6)	292.70	523.06
Xe	Stephen <i>et al.</i> (1956)	3(3)	435.89	574.85
	Crovetto <i>et al.</i> (1982)	6(6)	295.39	465.96
D <sub>2</sub>	Scharlin and Battino (1992)	4(4)	288.17	318.10
	Stephen <i>et al.</i> (1956)	3(1)	435.89	574.85
	Morris <i>et al.</i> (2001)	10(10)	447.20	581.00
CH <sub>4</sub>	Scharlin and Battino (1992)	4(4)	288.16	318.16
	Crovetto <i>et al.</i> (1982)	8(8)	298.19	517.46

$$\mu_2^\infty(T) - \mu_2^\oplus(T) = RT \ln \frac{k_H}{p^\oplus}. \quad (6)$$

In this way, the mole fraction gas solubility can be related to the other quantities by

$$\ln x_2 = \ln \frac{y_2 \phi_2 p}{\gamma_2^H k_H} - \int_{p_1^*}^p \frac{V_2^\infty}{RT} dp. \quad (7)$$

Combining Eqs. (4) and (7), the full expression for  $k_H$  is obtained:

$$k_H = \frac{\phi_2 p}{x_2 \gamma_2^H} \exp\left(-\int_{p_1^*}^p \frac{V_2^\infty}{RT} dp\right) \left[1 - \frac{\phi_1^* p_1^*}{\phi_1 p} \exp\int_{p_1^*}^p \frac{V_1^*}{RT} dp\right]. \quad (8)$$

If we take  $x_2 \rightarrow 0$  in Eq. (7), so that  $p \rightarrow p_1^*$ ,  $\gamma_2^H \rightarrow 1$  and  $\phi_2 \rightarrow \phi_2^\infty$ , we get

$$k_H = \phi_2^\infty p_1^* \lim_{y_2, x_2 \rightarrow 0} \left(\frac{y_2}{x_2}\right). \quad (9)$$

Hence, from Eq. (2)

$$k_H = \phi_2^\infty p_1^* K_D. \quad (10)$$

The procedure employed in this work has been to calculate  $k_H$  from the experimental data ( $p, T, x_2$ ) and then obtain  $K_D$  from Eq. (10). The primary expression to calculate Henry's constant from the data is Eq. (8); several factors in this equation require comments. The Peng-Robinson (1976, 1980) equation of state has been used to calculate the fugacity coefficients together with Eq. (4) to determine the gas-phase composition. Apart from the three experimentally determined quantities ( $p, T, x_2$ ), it is necessary to calculate the fugacity coefficients, the Poynting corrections

$$\exp\left(-\int_{p_1^*}^p \frac{V_2^\infty}{RT} dp\right)$$

and the corrections for solute-solute interactions that are reflected in  $\gamma_2^H$ . These last two corrections are small at low

temperatures, and the latter is even negligible below 523 K for most slightly soluble gases, but at high temperatures they cannot be neglected. The reason these two correction terms become important at high temperatures is that both  $V_2^\infty$  and  $\gamma_2^H$  diverge to infinity at the critical point of the solvent (Fernández-Prini and Japas, 1994).

There were exceptions to the calculation procedure described above for some data sets. Most notably, for the solutes CO<sub>2</sub> and H<sub>2</sub>S, which are much more soluble than the other gases we considered, the activity coefficient  $\gamma_2^H$  affects the data at much lower temperatures due to larger values of  $x_2$  and therefore could not be neglected even at the lower temperatures where it was neglected for other solutes.

### 3.2. Data Processing

The input used to calculate  $k_H$  was the set of experimental  $p, T, x_2$  values; whenever these three variables were not directly reported by the authors, they were calculated from the information provided in the sources. The Peng-Robinson (1976, 1980) equation of state was used to calculate the fugacity coefficient in the vapor phase for the mixtures with the mixing parameters reported by Fernández-Prini and Crovetto (1989). For the gases that were not analyzed in that article (CO, CO<sub>2</sub>, H<sub>2</sub>S, SF<sub>6</sub>), the  $\delta_{ij}$  mixing parameter was taken as 0.5, which was the value observed for the majority of the gas-water systems studied previously.

For those gases whose solubility has been reported over a range of pressure at each temperature,  $k_H$  could be calculated by extrapolation as suggested by its definition in Eq. (1), although it is often observed that in these cases the data cannot be extrapolated with sufficient precision to determine  $k_H$  accurately. On the other hand, the majority of the gas solubility data available in the literature correspond to single points at each temperature, so that extrapolation cannot be used as a general procedure to calculate  $k_H$ . Therefore, it is necessary to calculate Henry's constant with Eq. (8). In order to use this equation, it is necessary to calculate the corrections included in the right side of Eq. (8). This requires knowledge of both the partial molar volume of the solutes at infinite dilution,  $V_2^\infty$ , and the activity coefficient of the solute,  $\gamma_2^H$ . Calculation of these two corrections is described in Appendix A.

For the systems for which isothermal solubilities exist over a pressure range, with the exception of CO<sub>2</sub> and H<sub>2</sub>S (see below), we used Eq. (8) to calculate  $k_H$  from the solubility data at each pressure; the average values of  $k_H$  at each temperature were used as input in the fitting procedure. As will be discussed in Section 3.4, in all cases we have checked the consistency of the fitted data with the known asymptotic relation for  $K_D$  and also, when possible, with an alternative procedure to calculate the equilibrium distribution constant of the gaseous solutes.

Whenever the high-temperature experimental method was used to study the more soluble gases, the correction for the solute's activity coefficient was significant in comparison with the experimental uncertainty at all temperatures. In the

present work, there were two gases of this type: CO<sub>2</sub> and H<sub>2</sub>S. We dealt with each of these binary systems in a different manner because there are many more data for CO<sub>2</sub> than for H<sub>2</sub>S. For carbon dioxide, there are several sets of data at low temperature, but, with the exception of the studies of Morrison and Billett (1952) and Murray and Riley (1971), the solubilities have been measured employing large values of  $p_2$  typical of the high-temperature method, implying a larger value of  $x_2$ . Under these experimental conditions,  $\gamma_2^H$  could not be neglected even at low temperatures. It is convenient to define  $Y$  through

$$\ln Y = \ln k_H + \ln \gamma_2^H, \quad (11)$$

so that  $Y$  differs from Henry's constant because it is not corrected for the nonideal behavior of the solute in the liquid phase. For CO<sub>2</sub>,  $Y$  was calculated from isothermal solubilities and fitted to Eq. (11) by employing a simple three-term polynomial in temperature for the coefficient  $b(T)$  of Eq. (A1). This polynomial was employed to correct all the values of  $Y$  for aqueous CO<sub>2</sub>.

In the case of H<sub>2</sub>S, there are few data, especially at high temperatures, so we have used the extrapolated values of  $k_H$  reported by Lee and Mather (1977) and the few data at higher temperatures from Gillespie and Wilson (1982), which we extrapolated to  $p_2=0$ .

Values for all properties of pure H<sub>2</sub>O needed for processing the data were taken from the NIST database for water properties (Harvey *et al.*, 2000). The vapor pressure of D<sub>2</sub>O was taken from Harvey and Lemmon (2002), while the other thermodynamic properties of D<sub>2</sub>O were computed from the equation of state of Hill *et al.* (1982).

### 3.3. Low-Temperature Data

The corrections required to calculate  $k_H$  from solubility data at low temperatures and pressures (i.e., employing the low-temperature method) are small and relatively simple to deal with; the activity coefficient of the solutes in the solution can usually be ignored. However, for those low-temperature data taken with high-precision apparatus, vapor fugacity corrections are significant compared to the precision of the data. Fortunately, in almost all cases the authors of these studies had already made a vapor fugacity correction, so we took their reported Henry's constants directly. For the few remaining systems, we applied the Peng-Robinson equation as described in the previous section.

### 3.4. Asymptotic Behavior and Consistency Verification

To obtain formulations that can be extrapolated with some confidence beyond the experimental temperature range, it is important to have asymptotic relationships for  $k_H$  and  $K_D$ . Experimental data in the near-critical range are scarce and have larger uncertainties, and in that region the solubilities depend strongly on temperature. Japas and Levelt Sengers (1989) derived the asymptotic density and temperature de-

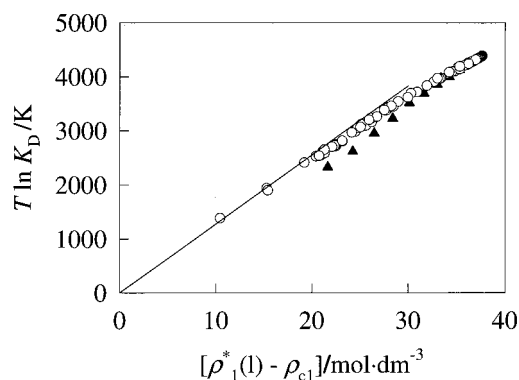


Fig. 1.  $T \ln K_D$  for H<sub>2</sub> in H<sub>2</sub>O as a function of  $[\rho_1^*(1) - \rho_{c1}]$ . Open symbols correspond to data used in the correlation, ( $\blacktriangle$ ) to those of Jung (1968; Jung *et al.*, 1971) which were not included. The straight line is the limiting slope related to the Krichevskii parameter as given by Eq. (13).

pendence of  $\ln k_H$  and  $\ln K_D$ . This was an important contribution to establish the most useful functional form for correlating these two quantities. The asymptotic equations they derived are linear in the density of the saturated liquid solvent  $\rho_1^*(1)$ :

$$RT \ln \left( \frac{k_H}{f_1^*} \right) = C_1 + \frac{1}{(\rho_{c1})^2} \left( \frac{\partial p}{\partial x_2} \right)_{T,V}^{\infty,c} [\rho_1^*(1) - \rho_{c1}], \quad (12)$$

$$RT \ln K_D = \frac{2}{(\rho_{c1})^2} \left( \frac{\partial p}{\partial x_2} \right)_{T,V}^{\infty,c} [\rho_1^*(1) - \rho_{c1}]. \quad (13)$$

$C_1$  is the derivative (at constant  $T$  and  $V$ ) of the residual Helmholtz energy (the nonideal part of the Helmholtz energy) with respect to  $x_2$  at the critical point, and  $\rho_{c1}$  is the critical density of the solvent. Japas and Levelt Sengers (1989) observed that, for aqueous and nonaqueous binary solutions, the linearity extended for an unexpectedly large range; since then, this feature has been verified for many systems (Harvey and Levelt Sengers, 1990; Alvarez *et al.*, 1994). Equations (12) and (13) provide important means of describing the thermodynamic properties of solutes at infinite dilution near the solvent's critical point. Equation (13) has the added advantage that  $\ln K_D$  must be zero at  $T_{c1}$ , giving an exact point for the extrapolation of data to the solvent critical point. The derivative  $(\partial p / \partial x_2)_{T,V}^{\infty,c}$  in Eqs. (12) and (13), known as the Krichevskii parameter, is taken at infinite dilution at the critical point of the solvent.

Equation (13) has proved very useful in evaluating some data. Figure 1 illustrates the case of the H<sub>2</sub>-H<sub>2</sub>O binary system, where the data of Jung (1968; Jung *et al.*, 1971) are shown not to extrapolate to the limit  $T \ln K_D = 0$  as they should (and as other data do); this led us to disregard those data.

For those systems for which there were good phase-diagram studies, we made use of another thermodynamic relationship to verify the consistency of the calculations of  $k_H$  and  $K_D$ . This relationship connects  $K_D$  to the change of pres-

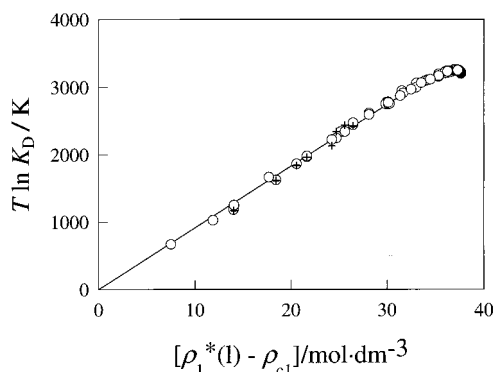


FIG. 2.  $T \ln K_D$  as a function of  $[\rho_1^*(l) - \rho_{c1}]$  for the  $\text{CO}_2\text{-H}_2\text{O}$  system: (O) calculated from Eq. (8) and (+) calculated from Eq. (14). The straight line is the asymptotic slope.

sure with composition along an isothermal vapor-liquid coexistence curve; it is derived without any simplifying assumptions. The resulting equation is (Alvarez *et al.*, 1994)

$$K_D = 1 + \frac{V_1^*(g) - V_1^*(l)}{RT} \left( \frac{\partial p}{\partial x_2} \right)_{T,\sigma}^{\infty} \quad (14)$$

In order to use Eq. (14) to calculate  $K_D$ , it is necessary to know  $(\partial p / \partial x_2)_{T,\sigma}^{\infty}$ , where subscript  $\sigma$  indicates that the derivative is taken along the curve of phase coexistence. Equation (14) has the advantage of being free from any approximations or models, so that if the data allow a proper extrapolation of  $(\partial p / \partial x_2)_{T,\sigma}$  to infinite dilution, Eq. (14) will yield the correct value of the distribution constant. Taking into account the uncertainty of the vapor-liquid equilibrium data and the precision of the extrapolation of  $(\partial p / \partial x_2)_{T,\sigma}$ , the values of  $K_D$  obtained with this procedure generally have a larger uncertainty than those calculated with the procedure that makes use of Eq. (8).

We have applied Eq. (14) to those systems for which there is sufficient information to calculate  $(\partial p / \partial x_2)_{T,\sigma}$ ; the values of  $K_D$  obtained in this way were employed only as a guide and were not included in the  $K_D$  data to be fitted. Figure 2 illustrates for the system  $\text{CO}_2\text{-H}_2\text{O}$  the agreement between the values of  $K_D$  obtained from  $k_H$  and those calculated with Eq. (14); there is good consistency between the values obtained from the complete thermodynamic treatment of solubilities and those calculated from phase-diagram information. Equation (14), along with the asymptotic relationship given by Eq. (13), have been very important for discriminating among discrepant sets of data and for validating the calculations of  $k_H$  from gas solubilities from Eq. (8).

For the purpose of the present work, the use of the asymptotic relationship given by Eq. (13) has even enabled us to decide the most adequate formulation in cases where there are no data above, say, 520 K where the linear relation is valid; examples were the solutions of the gases  $\text{CO}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{SF}_6$ .

## 4. Fitting Procedure

Henry's constants were fitted to the equation proposed by Harvey (1996):

$$\ln(k_H/p_1^*) = A/T_R + \frac{B\tau^{0.355}}{T_R} + C(T_R)^{-0.41} \exp \tau, \quad (15)$$

where  $\tau = 1 - T_R$ ,  $T_R = T/T_{c1}$ ,  $T_{c1}$  is the critical temperature of the solvent as accepted by IAPWS (1995b) (647.096 K for  $\text{H}_2\text{O}$ , 643.847 K for  $\text{D}_2\text{O}$ ), and  $p_1^*$  is the vapor pressure of the solvent at the temperature of interest.  $p_1^*$  is calculated from the correlation of Wagner and Pruss (1993) for  $\text{H}_2\text{O}$  and from the correlation of Harvey and Lemmon (2002) for  $\text{D}_2\text{O}$ .

Vapor-liquid distribution coefficients were fitted to the equation proposed by Alvarez *et al.* (1994)

$$\ln K_D = qF + \frac{E}{T/K} f(\tau) + (F + G\tau^{2/3} + H\tau) \times \exp\left(\frac{273.15 - T/K}{100}\right). \quad (16)$$

The value of the constant  $q$  is determined by the requirement that  $\ln K_D = 0$  at  $T = T_{c1}$ ;  $q$  is  $-0.023767$  for  $\text{H}_2\text{O}$  and  $-0.024552$  for  $\text{D}_2\text{O}$ . The coefficient  $E$  is related to the Krichevskii parameter by

$$E = \frac{2}{R\rho_{c1}} \left( \frac{\partial p}{\partial x_2} \right)_{T,V}^{\infty,c}$$

In Eq. (16),  $f(\tau) = (\rho_1^*(l)/\rho_{c1}) - 1$  gives the relation between the liquid density and the temperature at saturation. For  $\text{H}_2\text{O}$ , this is given by Wagner and Pruss (1993). For  $\text{D}_2\text{O}$ , no equation for  $f(\tau)$  was available, so we fit an equation to the saturated densities given by Hill *et al.* (1982); the resulting equation is

$$f(\tau)[\text{D}_2\text{O}] = a_1\tau^{0.374} + a_2\tau^{1.45} + a_3\tau^{2.6} + a_4\tau^{12.3}, \quad (17)$$

with  $a_1 = 2.7072$ ,  $a_2 = 0.58662$ ,  $a_3 = -1.3069$ , and  $a_4 = -45.663$ .

To begin the fitting process, data were divided into two categories: "low-temperature" data at and below 333.15 K, and "high-temperature" data above that temperature. This division is arbitrary, but was convenient because it placed all the highly precise solubility data in the "low-temperature" category.

All  $k_H$  points for a given solute in a solvent were fitted simultaneously to Eq. (15). In cases where there were many more data points at low temperatures than at high temperatures, the low-temperature points were given a smaller weight to keep them from dominating the fit; the smaller weight was chosen in these cases so that the total weights of the low-temperature and high-temperature points were simi-



TABLE 3. Parameters for correlation of Henry's constants in H<sub>2</sub>O with Eq. (15)

Solute	A	B	C	T <sub>min</sub> /K	T <sub>max</sub> /K
He	-3.528 39	7.129 83	4.477 70	273.21	553.18
Ne	-3.183 01	5.314 48	5.437 74	273.20	543.36
Ar	-8.409 54	4.295 87	10.527 79	273.19	568.36
Kr	-8.973 58	3.615 08	11.299 63	273.19	525.56
Xe	-14.216 35	4.000 41	15.609 99	273.22	574.85
H <sub>2</sub>	-4.732 84	6.089 54	6.060 66	273.15	636.09
N <sub>2</sub>	-9.675 78	4.721 62	11.705 85	278.12	636.46
O <sub>2</sub>	-9.448 33	4.438 22	11.420 05	274.15	616.52
CO	-10.528 62	5.132 59	12.014 21	278.15	588.67
CO <sub>2</sub>	-8.554 45	4.011 95	9.523 45	274.19	642.66
H <sub>2</sub> S	-4.514 99	5.235 38	4.421 26	273.15	533.09
CH <sub>4</sub>	-10.447 08	4.664 91	12.129 86	275.46	633.11
C <sub>2</sub> H <sub>6</sub>	-19.675 63	4.512 22	20.625 67	275.44	473.46
SF <sub>6</sub>	-16.561 18	2.152 89	20.354 40	283.14	505.55

lar. The fitting procedure minimized the sum of squares of the deviations between experimental and predicted values of  $\ln k_H$ .

After each fit, the root-mean-square deviations (RMSDs) of the low- and high-temperature data were computed separately. Points in those regions that deviated from the fit by more than twice the RMSD for the region were examined more closely; if removing a point significantly decreased the RMSD, it was rejected as an outlier. Tables 1 and 2 show the number of points from each experimental study accepted in the final fit.

For each system, the values of  $k_H$  included in the fit to Eq. (15) were converted into  $K_D$  with Eq. (10) and then fitted to Eq. (16) with a procedure analogous to that employed for Henry's constants.

## 5. Results and Discussion

Table 3 gives the parameters for the fits of  $k_H$  to Eq. (15) for solutes in H<sub>2</sub>O, along with the minimum and maximum temperatures covered by the fit. The RMSDs of the fits in the low- and high-temperature regions, along with the number of

TABLE 4. Root-mean-square deviations in  $\ln k_H$  for solutes in H<sub>2</sub>O and number of points in low-temperature and high-temperature regions of fit

Solute	RMSD <sub>low</sub>	N <sub>low</sub>	RMSD <sub>high</sub>	N <sub>high</sub>
He	0.0121	33	0.0341	7
Ne	0.0052	35	0.0577	8
Ar	0.0124	88	0.0443	7
Kr	0.0256	36	0.0434	9
Xe	0.0143	30	0.0363	10
H <sub>2</sub>	0.0123	16	0.0517	69
N <sub>2</sub>	0.0129	20	0.0372	47
O <sub>2</sub>	0.0128	35	0.0377	17
CO	0.0035	14	0.0039	3
CO <sub>2</sub>	0.0189	30	0.0528	50
H <sub>2</sub> S	0.0313	16	0.0408	11
CH <sub>4</sub>	0.0225	20	0.0386	25
C <sub>2</sub> H <sub>6</sub>	0.0147	34	0.0259	13
SF <sub>6</sub>	0.0344	14	0.0505	32

TABLE 5. Parameters for correlation of equilibrium distribution constants in H<sub>2</sub>O with Eq. (16)

Solute	E	F	G	H
He	2267.4082	-2.9616	-3.2604	7.8819
Ne	2507.3022	-38.6955	110.3992	-71.9096
Ar	2310.5463	-46.7034	160.4066	-118.3043
Kr	2276.9722	-61.1494	214.0117	-159.0407
Xe	2022.8375	16.7913	-61.2401	41.9236
H <sub>2</sub>	2286.4159	11.3397	-70.7279	63.0631
N <sub>2</sub>	2388.8777	-14.9593	42.0179	-29.4396
O <sub>2</sub>	2305.0674	-11.3240	25.3224	-15.6449
CO	2346.2291	-57.6317	204.5324	-152.6377
CO <sub>2</sub>	1672.9376	28.1751	-112.4619	85.3807
H <sub>2</sub> S	1319.1205	14.1571	-46.8361	33.2266
CH <sub>4</sub>	2215.6977	-0.1089	-6.6240	4.6789
C <sub>2</sub> H <sub>6</sub>	2143.8121	6.8859	-12.6084	0
SF <sub>6</sub>	2871.7265	-66.7556	229.7191	-172.7400

accepted points in each region, are given in Table 4. The same information is given in Tables 5 and 6 for the fits of  $K_D$  to Eq. (16). The minimum and maximum temperatures and number of low- and high-temperature points are not included in Tables 5 and 6 since they are identical to the values in Tables 3 and 4. In the remainder of this section, we will discuss the results in H<sub>2</sub>O by category of solute, followed by presentation and discussion of the results for solutes in D<sub>2</sub>O, followed by some comments on solutes that we did not include in this work.

### 5.1. Noble Gases in H<sub>2</sub>O

The solubilities of He, Ne, Ar, Kr, and Xe in H<sub>2</sub>O at low temperatures are all well determined by at least one thorough, high-quality experimental study. Equation (15) fits  $k_H$  for all these systems well at low temperatures, with the exception of krypton where the RMSD is worse by approximately a factor of 2.

At high temperatures, all the noble gases except for helium are covered by both the data of Potter and Clyne (1978) and of Crovetto *et al.* (1982). Unfortunately, these two sources are for the most part mutually inconsistent, re-

TABLE 6. Root-mean-square deviations in  $\ln K_D$  for solutes in H<sub>2</sub>O

Solute	RMSD <sub>low</sub>	RMSD <sub>high</sub>
He	0.0082	0.0316
Ne	0.0090	0.0590
Ar	0.0109	0.0220
Kr	0.0136	0.0314
Xe	0.0446	0.0313
H <sub>2</sub>	0.0064	0.0460
N <sub>2</sub>	0.0094	0.0400
O <sub>2</sub>	0.0133	0.0426
CO	0.0063	0.0312
CO <sub>2</sub>	0.0154	0.0439
H <sub>2</sub> S	0.0233	0.0375
CH <sub>4</sub>	0.0113	0.0348
C <sub>2</sub> H <sub>6</sub>	0.0222	0.0580
SF <sub>6</sub>	0.0230	0.0523

quiring us to make a (somewhat arbitrary) choice between them. Because Crovetto *et al.* (1982) give some reasons why the method of Potter and Clynne (1978) might be prone to error, we chose to use the data of Crovetto *et al.* (1982). With this choice, good fits at high temperature were obtained for all systems. However, it would be desirable for an independent experiment to verify which results are correct for one of these systems.

For helium in H<sub>2</sub>O, the only high-temperature data are from Potter and Clynne (1978). We therefore had no alternative but to use those data, and a good fit was achieved for both  $k_H$  and  $K_D$ . For the reasons given in the previous paragraph, some doubt must be attached to these results.

## 5.2. Diatomic Gases in H<sub>2</sub>O

For H<sub>2</sub>, our results are anchored at high temperatures by the data originally reported by Alvarez *et al.* (1988) and revised by Alvarez and Fernández-Prini (1991). With the exception of a few points from Pray *et al.* (1952), the only other data considered above 500 K were from Morris *et al.* (2001), who used a novel technique involving a palladium/hydrogen electrical resistance sensor. Their results show more scatter than most studies, but agree with the Alvarez data within their scatter. We therefore kept them in the fit, though several of the points were ultimately discarded as outliers. The relatively large RMS deviations reported in Tables 4 and 6 for H<sub>2</sub> at high temperatures are largely due to the scatter of the data of Morris *et al.* (2001). We also examined the data of Jung (1968; Jung *et al.*, 1971), but found that the solubility data along isotherms did not extrapolate to the  $T \ln K_D$  limit in a reasonable manner, as illustrated in Fig. 1. These data were therefore not included in the fit.

For N<sub>2</sub>, we also have thorough high-temperature data from Alvarez and Fernández-Prini (1991). All other studies [except for the precise low-temperature data of Rettich *et al.* (1984)] are considerably older, but for the most part in agreement.

For O<sub>2</sub>, there are only two high-temperature data sources, but the independent results of Stephen *et al.* (1956) and Cramer (1982) are in fairly good agreement.

For CO, there are precise low-temperature data (Rettich *et al.*, 1982), but the situation for high temperatures is not good. The CO data of Jung (1968; Jung *et al.*, 1971) were determined to be unsuitable for the same reasons as for H<sub>2</sub>. There are three solubility studies at moderate temperatures (near 400 K) from researchers studying carbonylation reactions in aqueous mixtures (Dake and Chaudhari, 1985; Taqui Khan and Halligudi, 1988; Taqui Khan *et al.*, 1989). Their results for CO solubility in pure H<sub>2</sub>O are wildly inconsistent with one another, so we did not use any of them. Finally, there are the data of Gillespie and Wilson (1980). This was an engineering study with less precision than many studies. For this reason, we chose not to use their data for other systems [H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> and CO<sub>2</sub> from Gillespie and Wilson (1982)] where we had a plentiful amount of data we considered to be superior. We did not have this luxury for

CO, so we processed their data at the five temperatures reported. The lowest temperature was in the range covered by Rettich *et al.* (1982); while reasonably consistent with those more precise data, the corresponding point was discarded as an outlier in the fitting process. A plot of  $T \ln K_D$  versus water density, like that shown in Fig. 1 for the H<sub>2</sub>-H<sub>2</sub>O system, suggested that the highest-temperature point was significantly in error, so it was discarded as well. The remaining three points provide the entire high-temperature basis for our correlation. The quite low RMS deviation reported in Table 4 is an artifact of the small number of points; the correlation for CO must be regarded as tentative due to the paucity of reliable data.

## 5.3. Other Solutes in H<sub>2</sub>O

The solubility of CO<sub>2</sub> in water has been extensively studied at all temperatures, but there are no high-precision values of  $k_H$  at low temperatures. This seemingly surprising situation can be attributed to the higher solubility of CO<sub>2</sub>, which requires corrections for the activity coefficient of the solute to derive  $k_H$  even when its partial pressure is near atmospheric pressure (this difficulty is even more acute for H<sub>2</sub>S). At high temperatures, there is some scatter among the different data sources, but we had no grounds for discarding any of them completely. This scatter, perhaps in part due to the increased difficulty of determining  $k_H$  for CO<sub>2</sub> from the experimental data because its solubility is greater, is reflected in the somewhat higher RMSD values for CO<sub>2</sub> compared to most other solutes.

For H<sub>2</sub>S, data of high accuracy extend only up to approximately 450 K (Lee and Mather, 1977). The data of Suleimenov and Krupp (1994) extend to high temperatures and were included in an earlier correlation (Harvey, 1996). However, analysis of the behavior of  $\ln K_D$  (similar to that shown in Fig. 1) strongly suggested a systematic problem with these data, so we did not include them. The high-temperature equilibrium compositions reported by Kozintseva (1964) appear reasonable, but the partial pressures tabulated in the paper are physically unrealistic. Because of this internal inconsistency, we chose not to use these data. That left the data of Gillespie and Wilson (1982), where the same concerns apply as for the Gillespie and Wilson (1980) CO data. Therefore, our results for H<sub>2</sub>S must be considered tentative above about 460 K. It is, however, encouraging that our correlated values of  $K_D$  appear consistent with the vapor and liquid compositions reported by Kozintseva (1964).

For both CO<sub>2</sub> and H<sub>2</sub>S, the weak ionization of the solute was ignored in all our work. This is a good assumption for solubility in neutral water, where the ionization is negligible for purposes of analyzing the experimental data. If one were considering the solubility of either of these weak acid gases in a basic solution, the ionic equilibria could not be ignored.

For CH<sub>4</sub>, data extend to quite high temperatures and there is fair consistency among various sources. For C<sub>2</sub>H<sub>6</sub>, almost all of the high-temperature data come from Crovetto *et al.* (1984). While these are described well by Eq. (15), they

TABLE 7. Parameters for correlation of Henry's constants in D<sub>2</sub>O with Eq. (15)

Solute	A	B	C	T <sub>min</sub> /K	T <sub>max</sub> /K
He	-0.726 43	7.021 34	2.044 33	288.15	553.18
Ne	-0.919 99	5.653 27	3.172 47	288.18	549.96
Ar	-7.177 25	4.481 77	9.315 09	288.30	583.76
Kr	-8.470 59	3.915 80	10.694 33	288.19	523.06
Xe	-14.464 85	4.423 30	15.609 19	295.39	574.85
D <sub>2</sub>	-5.338 43	6.157 23	6.530 46	288.17	581.00
CH <sub>4</sub>	-10.019 15	4.733 68	11.757 11	288.16	517.46

extend only to 473 K, so there is some uncertainty for this system in the values of  $k_H$  obtained with Eq. (15) for higher temperatures; this limitation is less severe for the case of  $K_D$  and Eq. (16), because the limiting value at  $T_{c1}$  is known.

For SF<sub>6</sub>, the only high-temperature data are those of Mroczek (1997). While they are fitted adequately, independent confirmation would be desirable. At low temperatures, the three temperature-dependent studies we considered differ by amounts on the order of 0.1 in  $\ln k_H$ . In order to choose among them, we first made use of the calorimetric data of Hallén and Wadsö (1989), whose enthalpies of solution may be compared with the temperature dependence of  $k_H$ . This comparison reveals that the temperature dependence of Morrison and Johnstone (1955) is clearly incorrect while the solubilities of Ashton *et al.* (1968) and Bullister *et al.* (2002) are reasonably consistent with the calorimetric data. These latter two sets are offset from one another, with Ashton *et al.* (1968) reporting higher solubilities. To choose between them, we made use of Park *et al.* (1982), who measured the solubility precisely at a single temperature near 25 °C. This datum for  $k_H$  agrees well with the Ashton data, but lies well below the Bullister data. When coupled with the principle that gas solubility data are more likely to be wrong in the direction of low solubility (higher  $k_H$ ), and the apparent agreement of the Ashton data with another study from Cosgrove and Walkley (1981) that we did not use because the data were not described unambiguously, we felt justified in excluding the data of Bullister *et al.* (2002). We therefore used only the low-temperature data of Ashton *et al.* (1968) and Park *et al.* (1982). It would be desirable if this system could be measured with modern high-precision techniques; experiments are likely more difficult for SF<sub>6</sub> because it is

TABLE 8. Root-mean-square deviations in  $\ln k_H$  for solutes in D<sub>2</sub>O and number of points in low-temperature and high-temperature regions of fit

Solute	RMSD <sub>low</sub>	N <sub>low</sub>	RMSD <sub>high</sub>	N <sub>high</sub>
He	0.0374	7	0.0341	5
Ne	0.0290	9	0.0355	6
Ar	0.0224	7	0.0452	10
Kr	0.0284	6	0.0178	4
Xe	0.0208	1	0.0524	6
D <sub>2</sub>	0.0372	4	0.0592	11
CH <sub>4</sub>	0.0235	6	0.0267	6

TABLE 9. Parameters for correlation of equilibrium distribution constants in D<sub>2</sub>O with Eq. (16)

Solute	E	F	G	H
He	2293.2474	-54.7707	194.2924	-142.1257
Ne	2439.6677	-93.4934	330.7783	-243.0100
Ar	2269.2352	-53.6321	191.8421	-143.7659
Kr	2250.3857	-42.0835	140.7656	-102.7592
Xe	2038.3656	68.1228	-271.3390	207.7984
D <sub>2</sub>	2141.3214	-1.9696	1.6136	0
CH <sub>4</sub>	2216.0181	-40.7666	152.5778	-117.7430

considerably less soluble than the other gases considered in this work.

The SF<sub>6</sub> data are not fitted well at the lowest temperatures (below about 285 K). This could mean that Eq. (15) is not well-suited to this system at low temperatures, but we also note that SF<sub>6</sub> readily forms a clathrate hydrate (Sortland and Robinson, 1964), and undetected hydrate formation could distort low-temperature solubility experiments.

#### 5.4. Solutes in D<sub>2</sub>O

Tables 7 and 8 give parameters and information about the fits for the correlation of  $k_H$  data to Eq. (15) for seven solutes in D<sub>2</sub>O. Tables 9 and 10 give the same information for the fits of  $K_D$  in D<sub>2</sub>O to Eq. (16).

At low temperatures, we made use of the Henry's constant data of Scharlin and Battino (1992) that exist for all solutes considered except xenon. These were not fitted quite as well as the low-temperature data for the same systems in H<sub>2</sub>O, but the fits were still adequate for our purposes. At high temperatures, the number of data points for each system considered was relatively small; the RMS deviations of the fits were similar to those for the solutes in H<sub>2</sub>O.

A system requiring further comment is D<sub>2</sub>/D<sub>2</sub>O, where the high-temperature data from Stephen *et al.* (1956) and Morris *et al.* (2001) differ significantly. There was no way to decide on the basis of these data alone which was correct. However, both of the studies in question also reported data for the H<sub>2</sub>/H<sub>2</sub>O system, where the data of Morris *et al.* (2001) appeared to be reliable while those of Stephen *et al.* (1956) deviated systematically from other studies and were discarded as outliers. On this basis, we discarded the two highest-temperature points from Stephen *et al.* (1956) for D<sub>2</sub>/D<sub>2</sub>O. As with H<sub>2</sub>/H<sub>2</sub>O, the data of Morris *et al.* (2001) have more scatter; this leads to higher RMSD values for

TABLE 10. Root-mean-square deviations in  $\ln K_D$  for solutes in D<sub>2</sub>O

Solute	RMSD <sub>low</sub>	RMSD <sub>high</sub>
He	0.0133	0.0241
Ne	0.0166	0.0184
Ar	0.0314	0.0410
Kr	0.0262	0.0068
Xe	0.0024	0.0480
D <sub>2</sub>	0.0558	0.0647
CH <sub>4</sub>	0.0109	0.0093

$D_2/D_2O$  in Tables 8 and 10. Correlation of this system is also made more difficult by the existence of a gap of over 100 K at intermediate temperatures where no data have been reported; see Table 2.

For the six gases studied in both  $H_2O$  and  $D_2O$  (He, Ne, Ar, Kr, Xe,  $CH_4$ ), we can examine the isotope effect of the solvent. At low and intermediate temperatures, all the gases have slightly smaller values of  $k_H$  (and are therefore slightly more soluble) in  $D_2O$ . At higher temperatures, this trend seems to reverse for some of the solutes, but it is difficult to tell within the uncertainty of the data and correlations whether this effect is real. A more detailed analysis of the differences between gas solubilities in  $H_2O$  and in  $D_2O$  at ambient temperatures has been given by Scharlin and Battino (1992).

### 5.5. Solute Excluded

There are several solutes for which some high-temperature solubility data in  $H_2O$  are available, but for which we did not produce correlations.

For ethene ( $C_2H_4$ ) and propene ( $C_3H_6$ ), high-temperature data were measured by Sanchez and Lentz (1973). However, analysis of these data revealed them to be inconsistent with the required asymptotic behavior (see Section 3.4), so the systems were not considered further.

For sulfur dioxide ( $SO_2$ ), several studies at moderately high temperatures exist, but the high solubility and reactivity of  $SO_2$  in water make it impossible to extract Henry's constants from the data with any confidence. Similarly, the high solubility of ammonia ( $NH_3$ ) in water meant that reliable Henry's constants could not be determined.

## 6. Conclusions

We have produced significantly improved correlations for both the Henry's constant  $k_H$  [Eq. (15)] and the vapor-liquid distribution constant  $K_D$  [Eq. (16)] for 14 solutes in  $H_2O$  and seven solutes in  $D_2O$ . These improvements result from better procedures to evaluate solubility data and from the incorporation of additional data. These formulations incorporate the correct asymptotic limiting laws as the critical temperature of the solvent is approached, allowing them to cover a very wide range of temperature and (especially in the case of  $K_D$ ) to be extrapolated beyond the experimental temperature range to the critical point of the solvent. These correlations are intended for those who need information at high temperatures or over a wide range of temperature; those who are concerned only with ambient temperatures should make use of the references for precise low-temperature data given in Tables 1 and 2.

There are a number of systems for which there is only a single source of experimental solubility data at high temperatures, or two sources that disagree; new experimental studies are encouraged for those systems. All of the  $D_2O$  systems are in that category, but since these are of more theoretical than practical interest, they are probably not the top priority. Of

the solutes in  $H_2O$  for which we correlated  $k_H$  and  $K_D$ , the ones of practical importance most in need of good high-temperature measurements in our opinion are  $H_2S$ ,  $C_2H_6$ ,  $O_2$ , and  $CO$ . In addition, there are important solutes ( $C_2H_4$ ,  $C_3H_8$ ,  $NH_3$ ,  $SO_2$ ) where the high-temperature data were inadequate for us to be able to produce even tentative correlations; these should also be priorities for future experimental work. Some systems ( $H_2$ ,  $CO_2$ ,  $H_2S$ , and  $SF_6$ ) also lack the kind of highly precise low-temperature data that exist for other common gases in water.

For those gases that are relatively soluble (such as  $CO_2$  and  $H_2S$ ), it is important to study isothermal solubilities at several different pressures in order to provide a sound means to determine  $k_H$  by extrapolation, since for these systems the corrections that can be applied to extract  $k_H$  from single data points for less soluble solutes are not reliable.

Whether it is more fruitful to approach a given practical problem by using values of  $k_H$  or  $K_D$  will depend in general on the vapor-liquid equilibrium conditions. If the vapor and liquid are very different (for example, if the solute mole fraction is near one in the vapor and near zero in the liquid), then  $k_H$ , with its asymmetric standard state, will usually be preferable. If the two phases are similar (for example, a high-temperature condition where the solute has a small mole fraction in both the vapor and liquid phases), then the quantity  $K_D$ , with its more symmetric definition, will usually be more convenient. When considering which approach to take, it may also be wise to consider the superior extrapolation capability of Eq. (16) for  $K_D$  at very high temperatures.

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## 8. Appendix A: Corrections to the Solute's Chemical Potential in the Liquid Phase

When gas solubilities have been determined with the high-temperature method (i.e.,  $p_2$  above about 0.5 MPa), the properties  $V_2^\infty$  and  $\gamma_2^H$  must be known to allow the determination of  $k_H$  at  $T$  and  $p_1^*$ , as shown by Eq. (8). The first exponential factor in Eq. (8), the Poynting effect on the solute, corrects  $\mu_2$  for the pressure in excess of  $p_1^*$ ; normally this correction cannot be neglected (within experimental uncertainty) at any temperature, but it is very large only when  $T \rightarrow T_{c1}$ . The correction factor  $\gamma_2^H$  is related to the excess chemical poten-

TABLE 11. Calculated values of  $\ln(k_H/1 \text{ GPa})$  for solutes at selected temperatures (in  $\text{H}_2\text{O}$  unless otherwise noted). Italics denote extrapolation beyond range of fitted data

Solute	300 K	400 K	500 K	600 K
He	2.6576	2.1660	1.1973	-0.1993
Ne	2.5134	2.3512	1.5952	0.4659
Ar	1.4061	1.8079	1.1536	0.0423
Kr	0.8210	1.4902	0.9798	0.0006
Xe	0.2792	1.1430	0.5033	-0.7081
H <sub>2</sub>	1.9702	1.8464	1.0513	-0.1848
N <sub>2</sub>	2.1716	2.3509	1.4842	0.1647
O <sub>2</sub>	1.5024	1.8832	1.1630	-0.0276
CO	1.7652	1.9939	1.1250	-0.2382
CO <sub>2</sub>	-1.7508	-0.5450	-0.6524	-1.3489
H <sub>2</sub> S	-2.8784	-1.7083	-1.6074	-2.1319
CH <sub>4</sub>	1.4034	1.7946	1.0342	-0.2209
C <sub>2</sub> H <sub>6</sub>	1.1418	1.8495	0.8274	-0.8141
SF <sub>6</sub>	3.1445	3.6919	2.6749	1.2402
He(D <sub>2</sub> O)	2.5756	2.1215	1.2748	-0.0034
Ne(D <sub>2</sub> O)	2.4421	2.2525	1.5554	0.4664
Ar(D <sub>2</sub> O)	1.3316	1.7490	1.1312	0.0360
Kr(D <sub>2</sub> O)	0.8015	1.4702	0.9505	-0.0661
Xe(D <sub>2</sub> O)	0.2750	1.1251	0.4322	-0.8730
D <sub>2</sub> (D <sub>2</sub> O)	1.6594	1.6762	0.9042	-0.3665
CH <sub>4</sub> (D <sub>2</sub> O)	1.3624	1.7968	1.0491	-0.2186

TABLE 12. Calculated values of  $\ln K_D$  for solutes at selected temperatures (in  $\text{H}_2\text{O}$  unless otherwise noted). Italics denote extrapolation beyond range of fitted data

Solute	300 K	400 K	500 K	600 K
He	15.2250	10.4364	6.9971	3.8019
Ne	15.0743	10.6379	7.4116	4.2308
Ar	13.9823	10.0558	6.9869	3.9861
Kr	13.3968	9.7362	6.8371	3.9654
Xe	12.8462	9.4268	6.3639	3.3793
H <sub>2</sub>	14.5286	10.1484	6.8948	3.7438
N <sub>2</sub>	14.7334	10.6221	7.2923	4.0333
O <sub>2</sub>	14.0716	10.1676	6.9979	3.8707
CO	14.3276	10.2573	7.1218	4.0880
CO <sub>2</sub>	10.8043	7.7705	5.2123	2.7293
H <sub>2</sub> S	9.6846	6.5840	4.2781	2.2200
CH <sub>4</sub>	13.9659	10.0819	6.8559	3.7238
C <sub>2</sub> H <sub>6</sub>	13.7063	10.1510	6.8453	3.6493
SF <sub>6</sub>	15.7067	11.9887	8.5550	4.9599
He(D <sub>2</sub> O)	15.2802	10.4217	7.0674	3.9539
Ne(D <sub>2</sub> O)	15.1473	10.5331	7.3435	4.2800
Ar(D <sub>2</sub> O)	14.0517	10.0632	6.9498	3.9094
Kr(D <sub>2</sub> O)	13.5042	9.7854	6.8035	3.8160
Xe(D <sub>2</sub> O)	12.9782	9.4648	6.3074	3.1402
D <sub>2</sub> (D <sub>2</sub> O)	14.3520	10.0178	6.6975	3.5590
CH <sub>4</sub> (D <sub>2</sub> O)	14.0646	10.1013	6.9021	3.8126

tial of the dissolved solute and will depend crucially on the solubility of the gas; it also becomes much larger as  $T_{c1}$  is approached. These corrections require knowledge of  $V_2^\infty$  and  $\gamma_2^H$  at every temperature and, for  $V_2^\infty$ , its value at all the pressures between  $p$  and  $p_1^*$ . Only for a very few systems is  $V_2^\infty$  known, and then only at a few temperatures; no measurements are available for the activity coefficients of gaseous solutes in water at high temperature. We have resorted to the use of a model and applied perturbation theory, in the Percus–Yevick approximation (Fernández-Prini *et al.*, 1992) for hard-sphere systems, to calculate  $V_2^\infty$  and  $\gamma_2^H$ . There is evidence that this approximation is good for  $V_2^\infty$  (Fernández-Prini and Japas, 1989), especially at high temperatures where the unusual behavior induced by hydrogen bonding in ambient water is not observed; the same model was used for calculation of  $\gamma_2^H$ . The equations used in the present work to calculate  $V_2^\infty$  and  $\gamma_2^H$  are given by Fernández-Prini *et al.* (1992) and by Alvarez and Fernández-Prini (1991), respectively. It should be remarked again that these equations, which depend on the hard-sphere equivalent diameter of the solutes  $d_2(T)$  and on the properties of water, are applicable primarily to systems at high temperatures, where the peculiar structural features of water do not contribute significantly to the properties of the solution.

With regard to the correction for the Poynting effect for the dissolved solute, as given by the first exponential term in Eq. (8), we have modified the procedure followed by Fernández-Prini and Crovetto (1989) in that we now have considered the dependence of  $V_2^\infty$  on the pressure in the integration; this dependence is mainly due to the variation of the density and compressibility of the solvent. The difference between the new and old procedures is appreciable only at

very high temperatures. The Poynting correction is always significant compared to the experimental uncertainty if the high-temperature methods ( $p_2 > 0.5 \text{ MPa}$ ) are used to determine the solubility of the gases.

To calculate  $\gamma_2^H$  for slightly soluble gases, it has been assumed in the present work that

$$\ln \gamma_2^H = b(T)x_2, \quad (\text{A1})$$

and  $b(T)$  was calculated from a model equation (Alvarez and Fernández-Prini, 1991) that depends on the hard-sphere equivalent diameter of the solute,  $d_2(T)$ . For slightly soluble gases, this correction is significant compared with the experimental uncertainty only above 523 K, increasing strongly as the temperature approaches  $T_{c1}$ .

The hard-sphere equivalent diameters of the solutes, on which the model equations for both corrections depend, were obtained with an iterative procedure at each temperature. The first guess for  $d_2$  was an approximate value of the Lennard-Jones diameter of each solute. With this value, the two corrections were calculated and the diameter adjusted until the value of Henry's constant calculated with the perturbation method agreed with the value obtained from the experimental solubility employing the complete Eq. (8). This procedure was applied at all temperatures and for all solutes, and the best linear or semilogarithmic fit of the hard-sphere diameter with temperature was obtained from them; these diameters were finally used for the corrections needed in Eq. (8).

Hence, the complete procedure employed for the calculation of  $k_H$  was self-consistent in the sense that the solute diameter  $d_2(T)$  was adjusted so that the values of Henry's constant, including the two corrections, could be described with Percus–Yevick first-order perturbation theory

(Fernández-Prini *et al.*, 1992). For all the binary systems that were studied by Fernández-Prini and Crovetto (1989), we have obtained the same temperature dependence for  $d_2$ . For SF<sub>6</sub>, the two corrections are small because the experimental solubilities are very small (Mroczek, 1997).

## 9. Appendix B: Values of $\ln k_H$ and $\ln K_D$ Calculated from the Correlations

Table 11 gives values of  $\ln k_H$  at 300, 400, 500, and 600 K calculated from Eq. (15) with the parameters given in Table 3 (for solutes in H<sub>2</sub>O) and Table 7 (for solutes in D<sub>2</sub>O). Similarly, Table 12 gives values of  $\ln K_D$  at the same temperatures calculated from Eq. (16) with the parameters given in Table 5 and Table 9. In both Tables 11 and 12, values are italicized if they are outside the limits of the data to which the correlation was fitted.

The number of digits given in these tables should not be taken as an indication of the uncertainty in the values; extra digits are given so that those who implement these correlations can verify their calculations. Section 5 and the tables therein should be consulted for information that may be used in estimating the uncertainties of calculated values.

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