# The International Association for the Properties of Water and Steam

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## Guideline on the Henry's Constant and Vapor-Liquid Distribution Constant for Gases in $H_2O$ and $D_2O$ at High Temperatures

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This guideline contains 9 pages, including this cover page.

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This guideline replaces the guideline "Solubility of simple apolar gases in light and heavy water at high temperature" issued in 1993 and the guideline "Guideline on the Equilibrium Constant for the Distribution of Gaseous Solutes between Steam and Water" issued in 1998.

Further information about this guideline and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS, or on the IAPWS Website at http://www.iapws.org.

# 1 Background

This guideline contains formulations for two closely related quantities concerning the solubility of gases in liquid water. The first quantity is the Henry's constant $k_H$, defined by

$$k_{\mathrm{H}} = \lim_{x_2 \to 0} \left( f_2 / x_2 \right) \tag{1}$$

where $f_2$ and $x_2$ are, respectively, the liquid-phase fugacity and mole fraction of the solute. While $k_H$ can be defined at any thermodynamic state point, in this guideline we only consider states on the solvent's vapor-liquid saturation boundary, making $k_H$ a function of temperature only. The second quantity is the vapor-liquid distribution constant $K_D$, defined by

$$K_{\mathrm{D}} = \lim_{x_2 \to 0} \left( y_2 / x_2 \right) \tag{2}$$

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

In 1993, IAPWS adopted a guideline for the representation of the Henry's constant $k_H$ over a wide range of temperatures for ten gases in $H_2O$ and seven gases in $D_2O$. In 1998, IAPWS adopted a guideline for the representation of the vapor-liquid distribution constant $K_D$ for ten solutes in $H_2O$. This guideline supersedes both of those documents, presenting formulations for both $k_H$ and $K_D$ that are based on a common, consistently evaluated data set and that take advantage of better data reduction techniques and an improved understanding of the high-temperature behavior of these properties. In the judgment of IAPWS, these formulations are the best available at the time of issue.

The background information for these formulations is given in Ref. [1]. All equations and coefficients needed for calculation of $k_H$ and $K_D$ are given in this document. Tables of calculated values are given for checking the implementation of these formulations.

# 2 Formulation for Henry's Constant

The Henry's constant $k_H$ is given as a function of temperature by

$$\ln\left(k_{\mathrm{H}} / p_1^*\right) = A / T_{\mathrm{R}} + \frac{B \tau^{0.355}}{T_{\mathrm{R}}} + C (T_{\mathrm{R}})^{-0.41} \exp \tau , \tag{3}$$

where $\tau = 1 - T_R$, $T_R = T / T_{c1}$, $T_{c1}$ is the critical temperature of the solvent as recommended by IAPWS [2] (647.096 K for $H_2O$, 643.847 K for $D_2O$), 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 [3] for $H_2O$ and from the correlation of Harvey and Lemmon [4] for $D_2O$. Both equations have the form

$$\ln\left(p_1^* / p_{\mathrm{c1}}\right) = T_{\mathrm{R}}^{-1} \sum_{i=1}^{n} a_i \tau^{b_i} , \tag{4}$$

where the number of terms $n$ is 6 for $H_2O$ and 5 for $D_2O$, $p_{c1}$ is the critical pressure of the solvent as recommended by IAPWS [2] (22.064 MPa for $H_2O$, 21.671 MPa for $D_2O$) and values of $a_i$ and $b_i$ are listed in Table 1.

Table 1. Coefficients for Eq. (4) for $H_2O$ and $D_2O$.

| $H_2O$ |  |  | $D_2O$ |  |
|---|---|---|---|---|
| $a_i$ | $b_i$ | $i$ | $a_i$ | $b_i$ |
| −7.859 517 83 | 1 | 1 | −7.896 657 | 1 |
| 1.844 082 59 | 1.5 | 2 | 24.733 08 | 1.89 |
| −11.786 649 7 | 3 | 3 | −27.811 28 | 2 |
| 22.680 741 1 | 3.5 | 4 | 9.355 913 | 3 |
| −15.961 871 9 | 4 | 5 | −9.220 083 | 3.6 |
| 1.801 225 02 | 7.5 | 6 |  |  |

Values of the coefficients *A*, *B*, and *C* in Eq. (3) for each system considered are listed in Table 2, along with the minimum and maximum temperatures of the data to which the correlations were fitted.

Table 2. Parameters for correlation of Henry's constants with Eq. (3). Solvent is $H_2O$ unless otherwise stated.

| Solute | *A* | *B* | *C* | $T_{\mathrm{min}}$/K | $T_{\mathrm{max}}$/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 |
| $H_2$ | −4.732 84 | 6.089 54 | 6.060 66 | 273.15 | 636.09 |
| $N_2$ | −9.675 78 | 4.721 62 | 11.705 85 | 278.12 | 636.46 |
| $O_2$ | −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 |
| $CO_2$ | −8.554 45 | 4.011 95 | 9.523 45 | 274.19 | 642.66 |
| $H_2S$ | −4.514 99 | 5.235 38 | 4.421 26 | 273.15 | 533.09 |
| $CH_4$ | −10.447 08 | 4.664 91 | 12.129 86 | 275.46 | 633.11 |
| $C_2H_6$ | −19.675 63 | 4.512 22 | 20.625 67 | 275.44 | 473.46 |
| $SF_6$ | −16.561 18 | 2.152 89 | 20.354 40 | 283.14 | 505.55 |
| He($D_2O$) | −0.726 43 | 7.021 34 | 2.044 33 | 288.15 | 553.18 |
| Ne($D_2O$) | −0.919 99 | 5.653 27 | 3.172 47 | 288.18 | 549.96 |
| Ar($D_2O$) | −7.177 25 | 4.481 77 | 9.315 09 | 288.30 | 583.76 |
| Kr($D_2O$) | −8.470 59 | 3.915 80 | 10.694 33 | 288.19 | 523.06 |
| Xe($D_2O$) | −14.464 85 | 4.423 30 | 15.609 19 | 295.39 | 574.85 |
| $D_2$($D_2O$) | −5.338 43 | 6.157 23 | 6.530 46 | 288.17 | 581.00 |
| $CH_4$($D_2O$) | −10.019 15 | 4.733 68 | 11.757 11 | 288.16 | 517.46 |

## 3 Formulation for Vapor-Liquid Distribution Constant

The vapor-liquid distribution constant $K_\mathrm{D}$ is given as a function of temperature by

$$\ln K_\mathrm{D} = qF + \frac{E}{T/\mathrm{K}} f(\tau) + (F + G\tau^{2/3} + H\tau)\exp\left(\frac{273.15 - \frac{T}{\mathrm{K}}}{100}\right), \tag{5}$$

where $f(\tau) = \left(\rho_1^*(\mathrm{l})/\rho_{\mathrm{c1}}\right) - 1$. $q$ is –0.023 767 when $H_2O$ is the solvent and –0.024 552 when $D_2O$ is the solvent. $\rho_1^*(\mathrm{l})$ is the liquid density along the vapor-liquid saturation boundary and $\rho_{\mathrm{c1}}$ is the critical density of the solvent. For $H_2O$, $f(\tau)$ is taken from Wagner and Pruss [3], while $f(\tau)$ for $D_2O$ was given by Fernández-Prini *et al.* [1]. In both cases, $f(\tau)$ has the following form:

$$f(\tau) = \sum_{i=1}^{n} c_i \tau^{d_i}, \tag{6}$$

where the number of terms $n$ is 6 for $H_2O$ and 4 for $D_2O$ and values of $c_i$ and $d_i$ are listed in Table 3. Note that the quantity required for Eq. (5) is the function $f(\tau) = \left(\rho_1^*(\mathrm{l})/\rho_{\mathrm{c1}}\right) - 1$; the value of $\rho_{\mathrm{c1}}$ itself is not needed.

Table 3. Coefficients for Eq. (6) for $H_2O$ and $D_2O$.

| $H_2O$ | | | $D_2O$ | |
|---|---|---|---|---|
| $c_i$ | $d_i$ | $i$ | $c_i$ | $d_i$ |
| 1.992 740 64 | 1/3 | 1 | 2.7072 | 0.374 |
| 1.099 653 42 | 2/3 | 2 | 0.586 62 | 1.45 |
| –0.510 839 303 | 5/3 | 3 | –1.3069 | 2.6 |
| –1.754 934 79 | 16/3 | 4 | –45.663 | 12.3 |
| –45.517 035 2 | 43/3 | 5 | | |
| $-6.746\,944\,5 \times 10^5$ | 110/3 | 6 | | |

Values of the coefficients *E*, *F*, *G* and *H* in Eq. (5) for each system considered are listed in Table 4. The minimum and maximum temperatures for these fits are identical to those listed in Table 2.

Table 4. Parameters for correlation of vapor-liquid distribution constants with Eq. (5). Solvent is $H_2O$ unless otherwise stated.

| 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 |
| $H_2$ | 2286.4159 | 11.3397 | –70.7279 | 63.0631 |
| $N_2$ | 2388.8777 | –14.9593 | 42.0179 | –29.4396 |
| $O_2$ | 2305.0674 | –11.3240 | 25.3224 | –15.6449 |
| CO | 2346.2291 | –57.6317 | 204.5324 | –152.6377 |
| $CO_2$ | 1672.9376 | 28.1751 | –112.4619 | 85.3807 |
| $H_2S$ | 1319.1205 | 14.1571 | –46.8361 | 33.2266 |
| $CH_4$ | 2215.6977 | –0.1089 | –6.6240 | 4.6789 |
| $C_2H_6$ | 2143.8121 | 6.8859 | –12.6084 | 0 |
| $SF_6$ | 2871.7265 | –66.7556 | 229.7191 | –172.7400 |
| He($D_2O$) | 2293.2474 | –54.7707 | 194.2924 | –142.1257 |
| Ne($D_2O$) | 2439.6677 | –93.4934 | 330.7783 | –243.0100 |
| Ar($D_2O$) | 2269.2352 | –53.6321 | 191.8421 | –143.7659 |
| Kr($D_2O$) | 2250.3857 | –42.0835 | 140.7656 | –102.7592 |
| Xe($D_2O$) | 2038.3656 | 68.1228 | –271.3390 | 207.7984 |
| $D_2$($D_2O$) | 2141.3214 | –1.9696 | 1.6136 | 0 |
| $CH_4$($D_2O$) | 2216.0181 | –40.7666 | 152.5778 | –117.7430 |

## 4 Range of Validity

The temperature range of validity for this Guideline can be considered to be the range of the data fitted, which is given in Table 2. In addition, the functional forms of the correlations are designed to obey the correct near-critical limiting forms. This means that they may be extrapolated to higher temperatures with some confidence, the level of confidence increasing the closer the data extend to the critical point. Extrapolation of $K_D$ is more reliable than extrapolation in $k_H$, because of the constraint that $K_D$ must have the value one at the critical temperature of the solvent.

It should be emphasized that these formulations are designed to cover a wide range of temperatures, up to the critical point of the solvent. While Eqs. (3) and (5) are fitted to low-temperature data as well, they do not describe the highly precise low-temperature data that exist for many systems to within their uncertainties. Those whose interest is confined to these low temperatures should not use the formulations in this guideline; instead they should use the data and smoothing equations in the papers reporting precise low-temperature data. These data sources are listed in Ref. [1].

## 5 Uncertainty

While a formal uncertainty analysis is impractical here, one can get an idea of the uncertainty in calculated values from the RMS (root-mean-square) deviations in the fits to the selected data. Table 5 gives the RMS deviations in fits to the selected high-temperature data (above 333.15 K) for both ln $k_H$ and ln $K_D$. Data selection criteria are given in Ref. [1]. It should be noted that, for some systems where data are sparse, the RMS deviation probably underestimates the true uncertainty. Reference [1] discusses the adequacy of the available data for various systems, and should be consulted for more complete information about the fits and additional information relevant to estimating uncertainties in these values.

Table 5. RMS Deviations for fits of ln $k_H$ [Eq. (3)] and ln $K_D$ [Eq. (5)] to selected high-temperature data.

| Solute | RMS Deviation in ln $k_H$ | RMS Deviation in ln $K_D$ |
|---|---|---|
| He | 0.0341 | 0.0316 |
| Ne | 0.0577 | 0.0590 |
| Ar | 0.0443 | 0.0220 |
| Kr | 0.0434 | 0.0314 |
| Xe | 0.0363 | 0.0313 |
| $H_2$ | 0.0517 | 0.0460 |
| $N_2$ | 0.0372 | 0.0400 |
| $O_2$ | 0.0377 | 0.0426 |
| CO | 0.0039 | 0.0312 |
| $CO_2$ | 0.0528 | 0.0439 |
| $H_2S$ | 0.0408 | 0.0375 |
| $CH_4$ | 0.0386 | 0.0348 |
| $C_2H_6$ | 0.0259 | 0.0580 |
| $SF_6$ | 0.0505 | 0.0523 |
| $He(D_2O)$ | 0.0341 | 0.0241 |
| $Ne(D_2O)$ | 0.0355 | 0.0184 |
| $Ar(D_2O)$ | 0.0452 | 0.0410 |
| $Kr(D_2O)$ | 0.0178 | 0.0068 |
| $Xe(D_2O)$ | 0.0524 | 0.0480 |
| $D_2(D_2O)$ | 0.0592 | 0.0647 |
| $CH_4(D_2O)$ | 0.0267 | 0.0093 |

## 6 Tabulated Values

For easy reference, and for the purpose of checking computer programs, Table 6 gives values of ln $k_H$ calculated from Eq. (3) at the temperatures 300 K, 400 K, 500 K, and 600 K. Values of ln $K_D$ at the same temperatures are given similarly in Table 7. In these tables, values are shown in italics if they are outside the range used to fit the correlation. The number of digits printed in Tables 6 and 7 does not indicate the uncertainty of the correlations; the previous section and Ref. [1] should be consulted for that information.

## 7 References

[1] Fernández-Prini, R., Alvarez, J., and Harvey, A.H., Henry's Constants and Vapor-Liquid Distribution Constants for Gaseous Solutes in $H_2O$ and $D_2O$ at High Temperatures, *J. Phys. Chem. Ref. Data*, 32, 903-916 (2003).

[2] IAPWS (International Association for the Properties of Water and Steam), Release on Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at Their Respective Critical Points. In *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry* (Proceedings, 12th International Conference on the Properties of Water and Steam), H.J. White, Jr., J.V. Sengers, D.B. Neumann, and J.C. Bellows, eds. (Begell House, New York, 1995), p. A101.

[3] Wagner, W., and Pruss, A., International Equations for the Saturation Properties of Ordinary Water Substance. Revised According to the International Temperature Scale of 1990., *J. Phys. Chem. Ref. Data*, 22, 783-787 (1993).

[4] Harvey, A.H., and Lemmon, E.W., Correlation for the Vapor Pressure of Heavy Water From the Triple Point to the Critical Point, *J. Phys. Chem. Ref. Data*, 31, 173-182 (2002).

Table 6. Calculated values of ln($k_H$/1 GPa) for solutes at selected temperatures (in $H_2O$ 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* |
| $H_2$ | 1.9702 | 1.8464 | 1.0513 | –0.1848 |
| $N_2$ | 2.1716 | 2.3509 | 1.4842 | 0.1647 |
| $O_2$ | 1.5024 | 1.8832 | 1.1630 | –0.0276 |
| CO | 1.7652 | 1.9939 | 1.1250 | *–0.2382* |
| $CO_2$ | –1.7508 | –0.5450 | –0.6524 | –1.3489 |
| $H_2S$ | –2.8784 | –1.7083 | –1.6074 | *–2.1319* |
| $CH_4$ | 1.4034 | 1.7946 | 1.0342 | –0.2209 |
| $C_2H_6$ | 1.1418 | 1.8495 | *0.8274* | *–0.8141* |
| $SF_6$ | 3.1445 | 3.6919 | 2.6749 | *1.2402* |
| He($D_2O$) | 2.5756 | 2.1215 | 1.2748 | *–0.0034* |
| Ne($D_2O$) | 2.4421 | 2.2525 | 1.5554 | *0.4664* |
| Ar($D_2O$) | 1.3316 | 1.7490 | 1.1312 | *0.0360* |
| Kr($D_2O$) | 0.8015 | 1.4702 | 0.9505 | *–0.0661* |
| Xe($D_2O$) | 0.2750 | 1.1251 | 0.4322 | *–0.8730* |
| $D_2$($D_2O$) | 1.6594 | 1.6762 | 0.9042 | *–0.3665* |
| $CH_4$($D_2O$) | 1.3624 | 1.7968 | 1.0491 | *–0.2186* |

Table 7. Calculated values of ln $K_\mathrm{D}$ for solutes at selected temperatures (in $H_2O$ 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* |
| $H_2$ | 14.5286 | 10.1484 | 6.8948 | 3.7438 |
| $N_2$ | 14.7334 | 10.6221 | 7.2923 | 4.0333 |
| $O_2$ | 14.0716 | 10.1676 | 6.9979 | 3.8707 |
| CO | 14.3276 | 10.2573 | 7.1218 | *4.0880* |
| $CO_2$ | 10.8043 | 7.7705 | 5.2123 | 2.7293 |
| $H_2S$ | 9.6846 | 6.5840 | 4.2781 | *2.2200* |
| $CH_4$ | 13.9659 | 10.0819 | 6.8559 | 3.7238 |
| $C_2H_6$ | 13.7063 | 10.1510 | *6.8453* | *3.6493* |
| $SF_6$ | 15.7067 | 11.9887 | 8.5550 | *4.9599* |
| He($D_2O$) | 15.2802 | 10.4217 | 7.0674 | *3.9539* |
| Ne($D_2O$) | 15.1473 | 10.5331 | 7.3435 | *4.2800* |
| Ar($D_2O$) | 14.0517 | 10.0632 | 6.9498 | *3.9094* |
| Kr($D_2O$) | 13.5042 | 9.7854 | 6.8035 | *3.8160* |
| Xe($D_2O$) | 12.9782 | 9.4648 | 6.3074 | *3.1402* |
| $D_2$($D_2O$) | 14.3520 | 10.0178 | 6.6975 | *3.5590* |
| $CH_4$($D_2O$) | 14.0646 | 10.1013 | 6.9021 | *3.8126* |