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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.

This guideline has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Kyoto, Japan, 29 August to 3 September, 2004, for issue by its Secretariat. The members of IAPWS are Argentina and Brazil, Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Italy, Japan, Russia, and the United States of America, and associate member Greece.

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

$$k_H = \lim_{x_2 \to 0} (f_2 / x_2) \tag{1}$$

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

$$K_D = \lim_{x_2 \to 0} (y_2 / x_2) \tag{2}$$

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

$$\ln(k_H / p_1^*) = A / T_R + \frac{B \tau^{0.355}}{T_R} + C(T_R)^{-0.41} \exp \tau, \tag{3}$$

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

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

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.

H₂O			D₂O	
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_{min}/K	T_{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
H₂	−4.732 84	6.089 54	6.060 66	273.15	636.09
N₂	−9.675 78	4.721 62	11.705 85	278.12	636.46
O₂	−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
CO₂	−8.554 45	4.011 95	9.523 45	274.19	642.66
H₂S	−4.514 99	5.235 38	4.421 26	273.15	533.09
CH₄	−10.447 08	4.664 91	12.129 86	275.46	633.11
C₂H₆	−19.675 63	4.512 22	20.625 67	275.44	473.46
SF₆	−16.561 18	2.152 89	20.354 40	283.14	505.55
He(D₂O)	−0.726 43	7.021 34	2.044 33	288.15	553.18
Ne(D₂O)	−0.919 99	5.653 27	3.172 47	288.18	549.96
Ar(D₂O)	−7.177 25	4.481 77	9.315 09	288.30	583.76
Kr(D₂O)	−8.470 59	3.915 80	10.694 33	288.19	523.06
Xe(D₂O)	−14.464 85	4.423 30	15.609 19	295.39	574.85
D₂(D₂O)	−5.338 43	6.157 23	6.530 46	288.17	581.00
CH₄(D₂O)	−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_D is given as a function of temperature by

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

(5)

where $f(\tau) = \left(\rho_1^*(l)/\rho_{c1}\right) - 1$. q is $-0.023\,767$ when H_2O is the solvent and $-0.024\,552$ when D_2O is the solvent. $\rho_1^*(l)$ is the liquid density along the vapor-liquid saturation boundary and ρ_{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:

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

(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 $f(\tau) = \left(\rho_1^*(l)/\rho_{c1}\right) - 1$; the value of ρ_{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 $\ln(k_H/1\ \mathrm{GPa})$ 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_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*