The International Association for the Properties of Water and Steam

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Revised Release on the Ionization Constant of H_2O

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This Revised Release replaces the corresponding Release of 2007, which replaced the Release "Ion Product of Water Substance" issued in 1980. It contains 7 pages, including this cover page.

This Revised Release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Banff, Canada, 29 September to 4 October, 2019. The members of IAPWS are: Australia, Britain and Ireland, Canada, the Czech Republic, Germany, Japan, New Zealand, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, and associate members Argentina and Brazil, China, Egypt, France, Greece, Italy, and Switzerland. The President at the time of adoption of this document was Dr. Jan Hrubý of the Czech Republic.

Summary

In this Revised Release, including the title, H_2O is used to refer to ordinary water substance. The equation for the ionization constant of water, K_w, provided in this release is a semi-empirical equation for K_w as a function of density and temperature. Details of the formulation can be found in the article "The Ionization Constant of Water over Wide Ranges of Temperature and Density" by A.V. Bandura and S.N. Lvov [1]. This equation represents values of $pK_w \equiv -\log_{10}(K_w)$ within experimental uncertainties for a temperature range from 25 °C to 800 °C and densities from 0 to 1.25 g cm^{-3}.

Further information about this Revised Release and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@iapws.org) or from http://www.iapws.org.

Contents

1 Nomenclature

Symbol	**Physical quantity**	**Unit**
a	activity (dimensionless). For ionic species (H^+, H_3O^+, OH^-), the standard state is the hypothetical ideally dilute solution at $m^0 = 1$ mol kg^{-1}. For H_2O, the standard state is pure H_2O at the same temperature and pressure.	
ρ	mass density	g cm^{-3}
ρ^0	normalizing mass density = 1 g cm^{-3}	g cm^{-3}
G	1000 g kg^{-1}	g kg^{-1}
K_w	ionization constant (dimensionless) of water at $m^0 = 1$ mol kg^{-1} (molal standard state)	
K_w^G	ionization constant (dimensionless) of water at $\rho = 0$ g cm^{-3} (ideal-gas standard state)	
M_w	molar mass of water = 18.015268 g mol^{-1}	g mol^{-1}
m^0	standard molality = 1 mol kg^{-1}	mol kg^{-1}
n	ion coordination number (dimensionless)	
p_s	vapor-liquid saturation pressure	MPa
t	Celsius temperature	°C
T	absolute temperature	K

2 Introductory Remark

This release presents an analytical equation for $\mathrm{p}K_\mathrm{w} \equiv -\log_{10}(K_\mathrm{w})$ over wide ranges of water density from 0 to 1.25 g cm^{-3} and temperature from 0 to 800 °C. The equation is based on comprehensive analysis of the experimental data collected, analyzed, and presented in Ref. [1].

3 The Ionization Constant Equation

The ionization constant of water is attributed to the following reaction:

$2H_2O \Leftrightarrow H_3O^+ + OH^-$.

Because the proton hydration is complete under all conditions of practical interest, this reaction may be used as a representative model for both liquid and vapor phases to the zero-density limit. Here and below, the molal standard state is used for the ionic species and mole-fraction standard state for water molecules. The ionization constant equation presented here is in a form which includes the equilibrium constant of the ionization reaction in the ideal-gas state, K_w^G. The ideal-gas ionization constant of water is calculated using the JANAF98 [2] data and then approximated by a temperature function:

$$\mathrm{p}K_\mathrm{w}^\mathrm{G} = \gamma_0 + \gamma_1 T^{-1} + \gamma_2 T^{-2} + \gamma_3 T^{-3}, \qquad (1)$$

where γ_0, γ_1, γ_2, γ_3 are empirical coefficients given in Table 1.

Based on the results given in Ref. [1], the ionization constant of water, K_w, as a function of temperature and density can be represented by the following equation:

$$\mathrm{p}K_\mathrm{w} = -2n\left[\log_{10}(1+Q) - \frac{Q}{Q+1}\rho(\beta_0 + \beta_1 T^{-1} + \beta_2\rho)\right] + \mathrm{p}K_\mathrm{w}^\mathrm{G} + 2\log_{10}\frac{m^0 M_\mathrm{w}}{G};, \qquad (2)$$

$$Q = (\rho/\rho^0)\exp(\alpha_0 + \alpha_1 T^{-1} + \alpha_2 T^{-2}\rho^{2/3}),$$

where M_w is the molar mass of water and α_0, α_1, α_2, β_0, β_1, β_2 are empirical parameters. The last term in Eq. (2) converts the ionization constant of water from the ideal-gas standard state (used for K_w^G) to the molal standard state (used for K_w).

In this formulation, K_w is defined as

$$K_\mathrm{w} = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{OH^-}}}{a_{\mathrm{H_2O}}^2}, \qquad (3)$$

where a_i is the dimensionless activity of the species i. Also, in this formulation it is assumed that the product of the activities of H^+ and H_2O is formally equal to the activity of H_3O^+ at any temperature and density (pressure), so that K_w is numerically equal to $\frac{a_{\mathrm{H^+}} a_{\mathrm{OH^-}}}{a_{\mathrm{H_2O}}}$, a thermodynamic constant for the ionization reaction of water ($H_2O \Leftrightarrow H^+ + OH^-$), that is most commonly used in the literature.

In Figure 1, the experimentally studied T-ρ regions are shown by both filled and open symbols. The filled symbols represent the data points used in the fit and the open symbols are the data which were not used in the fitting procedure due to larger uncertainties of the experimental studies carried out at very high pressure. The ion coordination number n was fixed at 6. The values obtained for α_0, α_1, α_2, β_0, β_1, and β_2 are given in Table 2.

Table 1. Empirical coefficients of Eq. (1)

Coefficient	Value	Units
γ_0	6.141500×10^{-1}	–
γ_1	4.825133×10^{4}	K
γ_2	-6.770793×10^{4}	K^2
γ_3	1.010210×10^{7}	K^3

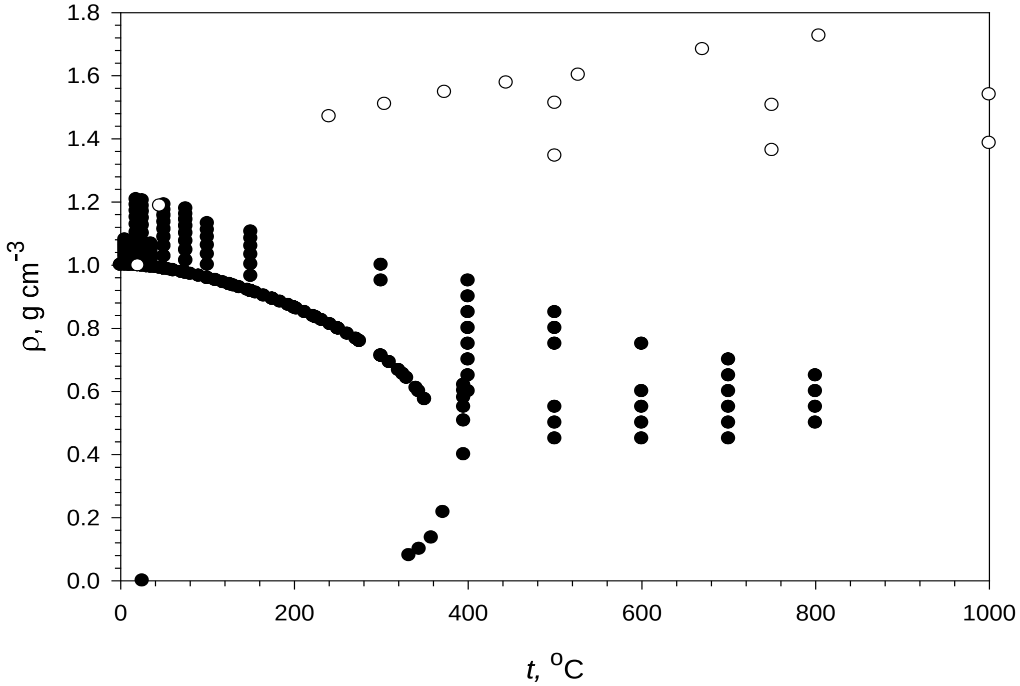

Figure 1. The temperature-density regions of the available experimental K_w data: ● - points used in the fitting procedure, ○ - points that were not used for fitting.

Table 2. Empirical coefficients of Eq. (2)

Coefficient	Value	Units
n	6	–
α_0	−0.864671	–
α_1	8659.19	K
α_2	−22786.2	$(\mathrm{g\ cm^{-3}})^{-2/3}\ \mathrm{K}^2$
β_0	0.642044	$(\mathrm{g\ cm^{-3}})^{-1}$
β_1	−56.8534	$(\mathrm{g\ cm^{-3}})^{-1}\ \mathrm{K}$
β_2	−0.375754	$(\mathrm{g\ cm^{-3}})^{-2}$

For the purpose of checking computer code, Table 3 contains calculated values of pK_w at specified temperatures and densities.

Table 3. Test values for calculating pK_w using Eqs. (1) and (2)

T, K	ρ, g cm^{-3}	pK_w
300	1.0	13.906565
600	0.07	21.048874
600	0.7	11.203153
800	0.2	15.089765
800	1.2	6.438330

4 Range of Validity and Estimates of Uncertainty

This release presents an analytical equation to calculate pK_w over wide ranges of water density from 0 to 1.25 g cm^{-3} and temperature from 0 to 800 °C. Values of pK_w calculated over a range of temperature (0-800 °C) and pressure (0.1-1000 MPa) using Eqs. (1) and (2), as well as the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [3, 4], are presented in Tables 4 and 5.

In the liquid-phase region and at moderate temperature (less than 200 °C) and pressure (less than 200 MPa), the deviations of the experimental data from the calculated values of pK_w do not generally exceed 0.05. Most of the available experimental data do not differ from those calculated by Eqs. (1) and (2) by more then the obtained standard deviation of 0.16. Deviations up to 0.8 in the low-density and supercritical regions are due to large experimental uncertainties at these state parameters. It is important to note that, in spite of the fact that the experimental high-pressure (up to 13 000 MPa) $\mathrm{p}K_\mathrm{w}$ values (shown in Figure 1 by open symbols) were not used in the fitting procedure, Eq. (2) can reproduce these data up to pressure of 13 000 MPa and density of 1.7 g cm^{-3} within 1.5. Note that the region of high temperature (above the critical point of water) and low density (below the critical density of water) has not been experimentally studied yet and more experiments are needed in this region to precisely define the uncertainty of $\mathrm{p}K_\mathrm{w}$ calculated in this region. The uncertainty of the calculated $\mathrm{p}K_\mathrm{w}^\mathrm{G}$, the ionization constant of water at $\rho = 0$ (ideal-gas state), is less than 0.005 in the whole temperature range up to 800 °C. For densities between the limit of experimental data (about 0.1 g cm^{-3}) and the ideal-gas limit, the physical basis for the interpolation provided by Eq. (2) is not rigorous. Therefore, quantitative accuracy cannot be expected in this region.

5 References

[1] Bandura, A.V., and Lvov, S.N., The Ionization Constant of Water over a Wide Range of Temperatures and Densities. *J. Phys. Chem. Ref. Data* **35**, 15-30 (2006).

[2] Chase, M.W., *JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data*, Monograph 9 (1998).

[3] IAPWS, R6-95(2018), *Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*, available from http://www.iapws.org/relguide/IAPWS-95.html.

[4] Wagner, W., and Pruß, A., The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **31**, 387-535 (2002).

Table 4. Negative logarithm (base 10) of the ionization constant of water, K_w, calculated at temperatures 0 to 300 °C and pressures 0.1 to 1000 MPa using Eqs. (1) and (2).

Pressure, MPa	Temperature, °C								
	0	25	50	75	100	150	200	250	300
0.1[a]	14.946[b]	13.995	13.264	12.696	12.252	11.641	11.310	11.205	11.339
25	14.848	13.908	13.181	12.613	12.165	11.543	11.189	11.050	11.125
50	14.754	13.824	13.102	12.533	12.084	11.450	11.076	10.898	10.893
75	14.665	13.745	13.026	12.458	12.006	11.364	10.974	10.769	10.715
100	14.580	13.668	12.953	12.385	11.933	11.283	10.880	10.655	10.568
150	14.422	13.524	12.815	12.249	11.795	11.135	10.713	10.458	10.327
200	14.278	13.390	12.687	12.123	11.668	11.000	10.564	10.289	10.131
250	14.145	13.265	12.567	12.004	11.549	10.876	10.430	10.140	9.963
300	14.021	13.148	12.453	11.892	11.437	10.760	10.306	10.005	9.814
350	13.906	13.037	12.346	11.786	11.331	10.651	10.191	9.881	9.679
400	13.797	12.932	12.243	11.685	11.230	10.548	10.083	9.766	9.555
500	13.595	12.736	12.052	11.496	11.042	10.356	9.884	9.557	9.332
600	13.411	12.556	11.875	11.322	10.868	10.181	9.703	9.369	9.135
700	13.240	12.389	11.710	11.159	10.705	10.018	9.537	9.197	8.956
800	13.080	12.233	11.556	11.006	10.553	9.865	9.381	9.037	8.791
900	12.930	12.085	11.410	10.861	10.410	9.721	9.236	8.888	8.638
1000	12.788	11.946	11.272	10.725	10.273	9.585	9.098	8.748	8.495

[a] 0.1 MPa at $t < 100$ °C and $t \geq 400$ °C, or p_s (saturated liquid) for 100 °C $\leq t \leq$ 350 °C

[b] Metastable liquid state

Table 5. Negative logarithm (base 10) of the ionization constant of water, K_w, calculated at temperatures 350 to 800 °C and pressures to 1000 MPa using Eqs. (1) and (2).

Pressure, MPa	Temperature, °C						
	350	400	450	500	600	700	800
0.1[a]	11.920	47.961	47.873	47.638	46.384	43.925	40.785
25	11.551	16.566	18.135	18.758	19.425	19.829	20.113
50	11.076	11.557	12.710	14.195	15.621	16.279	16.693
75	10.802	11.045	11.491	12.162	13.507	14.301	14.791
100	10.600	10.744	11.005	11.381	12.296	13.040	13.544
150	10.295	10.345	10.464	10.642	11.117	11.613	12.032
200	10.062	10.063	10.119	10.220	10.513	10.853	11.171
250	9.869	9.839	9.859	9.917	10.112	10.360	10.609
300	9.702	9.651	9.646	9.677	9.810	9.998	10.199
350	9.554	9.487	9.465	9.476	9.567	9.712	9.877
400	9.420	9.341	9.305	9.302	9.361	9.475	9.613
500	9.182	9.086	9.031	9.007	9.024	9.094	9.191
600	8.974	8.866	8.798	8.761	8.749	8.790	8.861
700	8.787	8.670	8.593	8.546	8.514	8.536	8.587
800	8.616	8.493	8.409	8.354	8.308	8.314	8.352
900	8.458	8.330	8.240	8.180	8.122	8.117	8.144
1000	8.311	8.178	8.084	8.019	7.952	7.939	7.957

[a] 0.1 MPa at $t < 100$ °C and $t \geq 400$ °C, or p_s (saturated liquid) for 100 °C $\leq t \leq$ 350 °C