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 Revised Release of 2019.
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 Boulder, Colorado, USA, 23–28 June, 2024. The members of IAPWS are: Australia, Britain and Ireland, Canada, Czechia, Germany and Switzerland, Japan, New Zealand, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, and associate members Argentina and Brazil, China, Egypt, France, Greece, India, Israel, and Italy. The President at the time of adoption of this document was Dr. Daniel G. Friend of the United States.

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, described in this release provides revised parameters for the semi-empirical equation developed by Bandura and Lvov [1] for K_w as a function of density and temperature. Details of the revised formulation can be found in the article "Revised Parameters for the IAPWS Formulation for the Ionization Constant of Water over a Wide Range of Temperatures and Densities, Including Near-Critical Conditions" by H. Arcis *et al.* [2]. This equation represents values of $pK_w \equiv -\log_{10}(K_w)$ within the expected experimental uncertainties for a temperature range from 0 °C to 1000 °C and pressure from 0 to 1000 MPa.

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

K_w	Ionization constant (dimensionless) of water at $m^0 = 1$ mol kg^{-1}
K_w^G	Ionization constant (dimensionless) of water at $\rho = 0$ g cm^{-3}
M_w	Molar mass of water, g mol^{-1} ($M_w = 18.015268$ g mol^{-1})
n	Ion coordination number parameter in Bandura–Lvov model
p	Pressure, MPa
p_{sat}	Vapor–liquid saturation pressure, MPa
T	Temperature, K
t	Temperature, °C
Z	Empirical function in Bandura–Lvov model, g cm^{-3}
α_i	Adjustable parameter in Bandura–Lvov model
β_i	Adjustable parameter in Bandura–Lvov model
ρ_w	Mass density, g cm^{-3}

2. Introductory Remark

This release presents revised parameters for the Bandura and Lvov (B-L) analytical equation for $pK_w \equiv -\log_{10}(K_w)$ [1] to cover wider ranges of temperature from 0 to 1000 °C and pressure from 0 to 1000 MPa. The revised equation is based on a comprehensive analysis of the experimental data which include new near-critical and supercritical flow conductivity data [3]. The data collection and analysis are presented in Ref. [2].

3. The Ionization Constant Equation

The equilibrium constant for the self-ionization of water, K_w, refers to the following reaction:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad (1)$$

The functional form of the equation presented below follows previous work from Bandura and Lvov [1], which formed the basis of the previous IAPWS Release [4]. The model uses the molal standard state for the ionic species and the mole-fraction standard state for water molecules, and the ionization constant of water is represented by the following equation:

$$\mathrm{p}K_\mathrm{w}(T,\rho_w) = -2n\left[\log_{10}(1+Z) - \frac{Z}{Z+1}\rho_\mathrm{w}\left(\beta_0 + \frac{\beta_1}{T} + \beta_2\rho_\mathrm{w}\right)\right] + \mathrm{p}K_\mathrm{w}^\mathrm{G}(T) + 2\log_{10}\frac{M_\mathrm{w}}{1000} \quad (2)$$

where Z is an empirical function of temperature and water density:

$$Z = \rho_\mathrm{w}\exp\left(\alpha_0 + \frac{\alpha_1}{T} + \frac{\alpha_2}{T^2}{\rho_\mathrm{w}}^{2/3}\right) \quad (3)$$

and where the equilibrium constant of the ionization reaction in the ideal-gas state, $\mathrm{p}K_\mathrm{w}^\mathrm{G}(T)$, is defined using reference thermodynamic data [5]:

$$\mathrm{p}K_\mathrm{w}^\mathrm{G}(T) = 0.61415 + \frac{48251.33}{T} - \frac{67707.93}{T^2} + \frac{10102100}{T^3} \quad (4)$$

In Eqs. (2), (3), and (4), T is the temperature in K, ρ_w is the water density in g cm^{-3}, $n = 6$ is the ion coordination number, M_w is the molar mass of water in g mol^{-1}, and α_0, α_1, α_2, β_0, β_1, and β_2 are fitted parameters given in Table 1.

Table 1. Parameters for Eq. (2).

Parameter	Value	Units
α_0	–0.702132	-
α_1	+8681.05	K
α_2	–24145.1	K^2 (g cm^{-3})$^{-2/3}$
β_0	+0.813876	cm^3 g^{-1}
β_1	–51.4471	K cm^3 g^{-1}
β_2	–0.469920	cm^6 g^{-2}

Figure 1 shows the temperature–density profile of the database used to regress the revised model parameters.

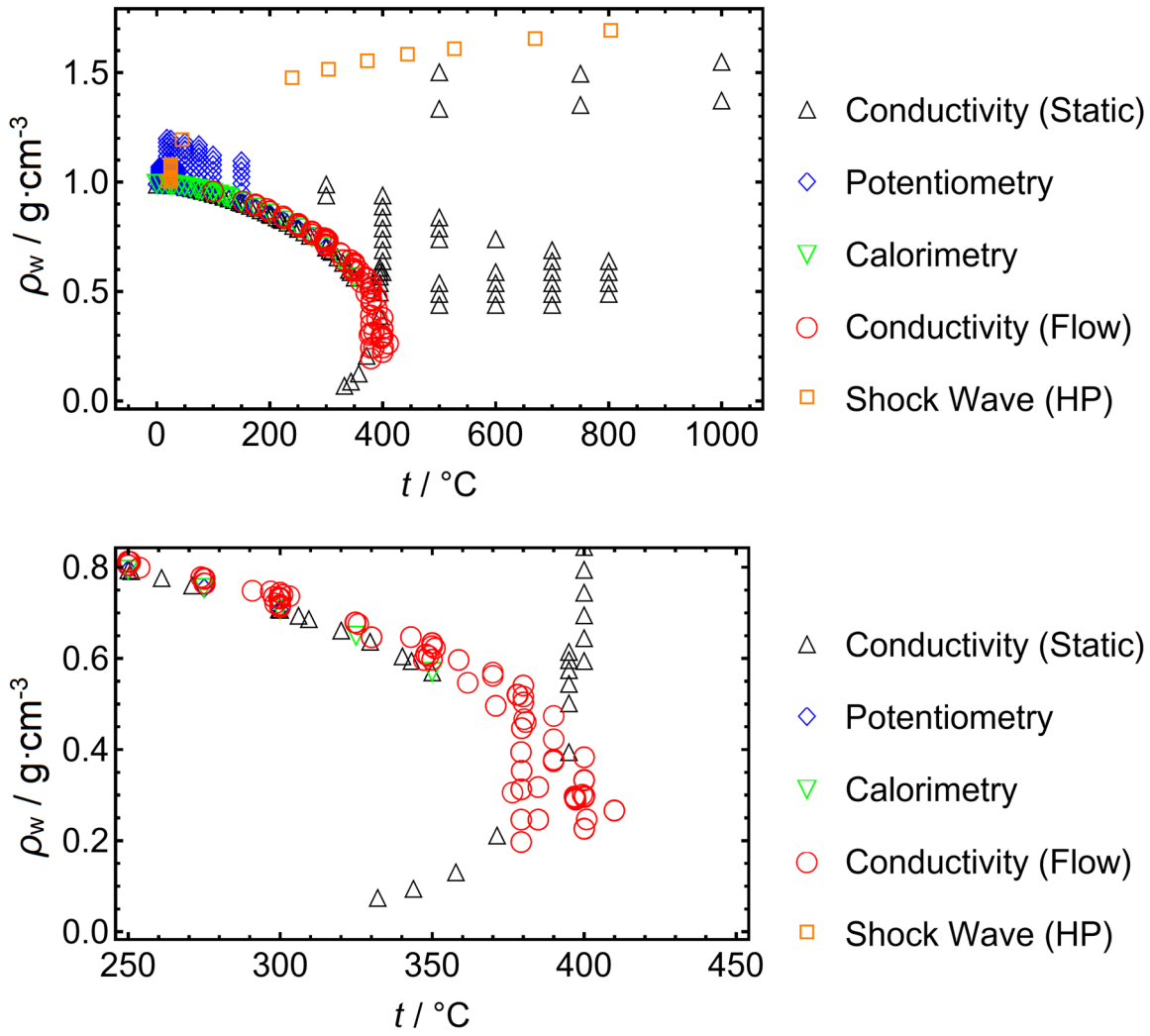

Figure 1. A temperature–density profile of the database used to regress the revised parameters listed in Table 1: Top, full experimental range; bottom, zoom illustrating knowledge gap filled at near-critical conditions.

For the purpose of checking computer code, Table 2 contains calculated values of pK_w at specified temperatures and densities. Extra digits are given for the purpose of program verification and do not reflect the uncertainties in pK_w (see Section 5).

Table 2. Test values for calculating pK_w using Eqs. (2), (3), and (4).

T / K	ρ_w / (g cm^{-3})	pK_w
300	1.0	13.906672
600	0.07	20.161651
600	0.7	11.147093
800	0.2	14.487671
800	1.2	6.4058649
1270	0.0	35.081557

4. Range of Validity

Equation (2) is recommended for computation of the ionization constant of water for all thermodynamically stable fluid states in the following ranges:

- 273.15 K ≤ T ≤ 1273.15 K;
- 0 MPa ≤ p ≤ 1000 MPa;

For general and scientific applications, the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [6,7] should be used to determine the densities as input to Eq. (2) when the state point under consideration is defined by pressure and temperature instead of density and temperature. In addition, IAPWS makes the following statements about the extrapolation of Eq. (2) outside the range of validity given above:

- Equation (2) provides reasonable extrapolation behavior for densities up to 1.69 g cm^{-3} at temperatures up to 1273 K. However, the recommended range of validity of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [6] only extends up to approximately 1.24 g cm^{-3};
- For stable fluid states outside the range of validity of Eq. (2), but within the range of validity of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [6], the extrapolation behavior of Eq. (2) is physically reasonable.

5. Estimates of Uncertainty

As for the previous release [4], 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. (2), (3), and (4) by more than the reported experimental uncertainties or errors. At near-critical conditions, only a few deviations between the calculated values and the experimental data are observed outside of the combined uncertainties, up to 0.77 pK units. The very high-pressure pK_w data up to 13 000 MPa and density of 1.69 g cm^{-3}, which are well outside range of validity of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [6], are reproduced within less than the expected experimental error of 3.0 pK units. The revised model is expected to be more accurate at near-critical and supercritical conditions due to the inclusion in the regression of flow conductivity data that filled the knowledge gap around the critical point. The uncertainty of the calculated pK_w^G , the ionization constant of water at $\rho_w = 0$ (ideal-gas state), remains less than 0.005 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.

6. Tabulated Values

Values of pK_w calculated over a range of temperature (0–1000 °C) and pressure (0.1–1000 MPa) using Eqs. (2), (3), and (4), as well as the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [6] to calculate the saturation pressure and the water density, are presented in Table 3.

Table 3. Calculated values of pK_w calculated at temperatures 0 °C to 1000 °C and pressures 0.1 MPa to 1000 MPa using Eqs. (2), (3), and (4).

Pressure	t / ºC																	
MPa	0 [a]	25	50	75	100	150	200	250	300	350	400	450	500	600	700	800	900	1000
p_{sat} [b]	14.95	13.99	13.26	12.70	12.25	11.64	11.31	11.19	11.29	11.77	-	-	-	-	-	-	-	-
15	14.89	13.94	13.21	12.65	12.20	11.59	11.24	11.11	11.20	18.99	20.07	20.54	20.85	21.28	21.58	21.80	21.94	21.97
25	14.85	13.91	13.18	12.61	12.17	11.55	11.19	11.04	11.09	11.45	15.88	17.35	17.95	18.60	18.99	19.28	19.49	19.61
50	14.76	13.83	13.10	12.54	12.09	11.46	11.08	10.90	10.87	11.02	11.42	12.40	13.68	14.97	15.58	15.97	16.25	16.45
75	14.67	13.75	13.03	12.46	12.01	11.37	10.98	10.77	10.71	10.77	10.97	11.33	11.89	13.03	13.73	14.17	14.48	14.71
100	14.58	13.67	12.95	12.39	11.94	11.29	10.89	10.66	10.57	10.58	10.69	10.91	11.21	11.96	12.59	13.03	13.34	13.57
150	14.42	13.52	12.82	12.25	11.80	11.14	10.72	10.47	10.34	10.29	10.32	10.42	10.56	10.94	11.34	11.67	11.94	12.15
200	14.28	13.39	12.69	12.12	11.67	11.01	10.58	10.30	10.15	10.07	10.06	10.10	10.18	10.41	10.67	10.92	11.13	11.31
250	14.14	13.26	12.56	12.00	11.55	10.88	10.44	10.16	9.98	9.88	9.85	9.86	9.90	10.05	10.24	10.43	10.60	10.75
300	14.02	13.14	12.45	11.89	11.44	10.77	10.32	10.02	9.83	9.72	9.67	9.66	9.68	9.78	9.92	10.08	10.22	10.34
350	13.90	13.03	12.34	11.78	11.33	10.66	10.20	9.90	9.70	9.58	9.51	9.48	9.49	9.55	9.67	9.79	9.91	10.02
400	13.79	12.92	12.23	11.68	11.23	10.55	10.09	9.78	9.58	9.44	9.37	9.33	9.32	9.36	9.45	9.56	9.66	9.75
500	13.58	12.72	12.04	11.48	11.03	10.36	9.89	9.57	9.35	9.21	9.11	9.06	9.04	9.04	9.10	9.17	9.26	9.33
600	13.39	12.54	11.86	11.30	10.85	10.17	9.71	9.38	9.15	9.00	8.90	8.83	8.79	8.78	8.81	8.87	8.93	9.00
700	-	12.36	11.68	11.14	10.69	10.01	9.53	9.20	8.97	8.81	8.70	8.63	8.58	8.55	8.57	8.61	8.66	8.72
800	-	12.20	11.52	10.98	10.53	9.85	9.37	9.04	8.80	8.64	8.52	8.44	8.39	8.35	8.35	8.39	8.43	8.48
900	-	12.04	11.37	10.82	10.38	9.70	9.22	8.89	8.64	8.47	8.35	8.27	8.21	8.16	8.16	8.19	8.22	8.27
1000	-	11.90	11.23	10.68	10.23	9.55	9.08	8.74	8.50	8.32	8.20	8.11	8.05	7.99	7.98	8.00	8.04	8.08

[a] Above $p \approx 629$ MPa, water at 0 °C is solid.

[b] Values generated using Eqs. (2), (3), (4) with the density of the liquid at 0.1 MPa below 100 °C, or the density of the saturated liquid at and above 100 °C.

7. References

[1] Bandura, A.V., and S.N. Lvov, The Ionization Constant of Water over Wide Ranges of Temperature and Density, *J. Phys. Chem. Ref. Data* **35**, 15 (2006).

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

[6] International Association for the Properties of Water and Steam, 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 at http://www.iapws.org/relguide/IAPWS-95.html.

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