A Revised Formulation for the Ionization Constant of Water over a Wide Range of Temperatures and Densities, Including Near-Critical Conditions

Hugues Arcis[1, S, C], Martin Bachet[2], Shirley Dickinson[3], Iain Duncanson[4], Richard Eaker[5], Jennifer Jarvis[4], Ken Johnson[6], Christopher Lee[3], Fred Lord[7], Chuck Marks[8] and Peter Tremaine[9]

[1]*Reactor Chemistry and Corrosion, National Nuclear Laboratory Limited, Abingdon, Oxfordshire, United Kingdom*
[2]*Department of Material and Mechanic of Component, EDF, Moret-Sur-Loing, France*
[3]*National Nuclear Laboratory Limited, Abingdon, Oxfordshire, United Kingdom*
[4]*Nuclear Fuels & Chemistry, Electric Power Research Institute, Charlotte, NC, U.S.A.*
[5]*HKA Enterprises, Duncan, SC, U.S.A.*
[6]*Electric Power Research Institute, Charlotte, NC, U.S.A.*
[7]*Materials, Chemistry and Corrosion, Rolls Royce PLC, London, United Kingdom*
[8]*Dominion Engineering, Inc., Reston, VA, U.S.A.*
[9]*Department of Chemistry, University of Guelph, Guelph, Ontario, Canada*
hugues.arcis@uknnl.com

The literature database for the ionization constant of water, $pK_{w,m}$, has been critically re-evaluated to include new accurate flow conductivity data recently reported at near-critical and supercritical conditions (Arcis et al. *J. Phys. Chem. Ref. Data* **2020**, 49, 033103). Revised equations to express the limiting conductivity of fully ionized water were used to correct the conductivity data and yield more accurate $pK_{w,m}$ values at water densities below 0.6 g cm^{-3}. The ability of the 1980 and 2006 IAPWS (International Association for the Properties of Water and Steam) functional forms to fit the near-critical and supercritical data were tested and revised parameters for the 2006 simple function were derived to improve the accuracy of the model under these conditions. The data fitting procedure made use of estimated errors as well as a weighting parameter for each dataset to minimize potential bias due to the very large amount of flow conductivity data available. Calculations based on the revised formulation were found to be consistent with independent high-temperature data measured using calorimetry and density methods. The revised equation can reproduce most of the literature data measured from 0 to 1000°C, p = 0.1 to 13,300 MPa, and from 0.08 to 1.69 g cm^{-3} to within their assigned errors.