ICRN 31

IAPWS Certified Research Need – ICRN

New Thermodynamic Data for Ordinary Water

The IAPWS Working Group "Thermophysical Properties of Water and Steam" has examined the published work and the experimental data available for thermodynamic properties of water, in order to facilitate the eventual development of an improved replacement for the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [1,2] and/or the Revised Release on the Surface Tension of Ordinary Water Substance [3]. Several areas have been identified where new, high-quality data, either from experiment or theory, are necessary in order to provide significant improvement over the existing formulation. In this ICRN, specific needs for further research are identified.

Although encouraging this work, IAPWS is not generally able to provide financial support. The IAPWS contacts can provide any further development information and will liaise between research groups.

Issued by the

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Background

In 1995, IAPWS approved a new formulation for the thermodynamic properties of water and steam, as documented in an IAPWS Release [1] and an archival journal article [2]. This formulation is commonly referred to as IAPWS-95. IAPWS-95 is recommended for calculating thermodynamic properties of ordinary water in the entire stable fluid region up to 1273.15 K and 1000 MPa.

For a variety of reasons, notably the availability of new experimental data and some shortcomings of the IAPWS-95 functional form, IAPWS is planning for the replacement of IAPWS-95 in the future. IAPWS has examined the currently available data, both data used for IAPWS-95 and new data reported since that time, and determined that additional measurements and theoretical calculations would be desirable in order to extend the range of applicability and reduce the uncertainty in calculated properties. Some needs were already stated in the recommendations of Section 9 of Ref. [2], but in the meantime additional needs have become evident and new data have satisfied some of the previously existing needs. Below, areas of need are outlined under the categories of experimental needs and needs in the area of theory and modeling. The list of data needs is not exhaustive, and the levels of required uncertainties are tentative. Researchers possessing or developing experimental or computational techniques which may potentially improve the data situation by providing smaller uncertainties and/or broader ranges of parameters are encouraged to consult the IAPWS contacts given at the end of this document for additional information and help.

Also, in 1976 IAPWS (then IAPS) issued a formulation for the vapor/liquid surface tension of ordinary water [3]. New experimental data would be useful for updating this correlation and improving its uncertainty estimates, and an item for this purpose has been included in the “Needs for Experimental Data” section below.

Needs for Experimental Data

Tentative uncertainties given here should be understood as expanded (k=2) combined uncertainties including uncertainties of independent experimental variables (*e.g.,* temperature and pressure).

- Accurate measurements of saturation vapor pressure above 373 K. The uncertainty of the measurements should be at most 0.02 %, but preferably less than 0.01 %. Similarly accurate measurements at temperatures below 373 K are also welcome to check the validity of existing data.

- Liquid densities at high temperatures (above approximately 400 K), especially near or at the vapor-liquid saturation boundary. These should preferably have uncertainties of 0.01 % or better.
- Vapor densities at high temperatures (above approximately 500 K), especially near or at the vapor-liquid saturation boundary. These should preferably have uncertainties of 0.03 % or better.
- Data (density, heat capacity, and/or sound speed) for the metastable subcooled vapor. Data in this region should be more accurate than extrapolation based on a truncated virial equation of state using quantum-mechanical values of the second virial coefficient.
- Density data at temperatures above 800 K.
- Density data at pressures above 100 MPa.
- Density data near the vapor-liquid critical point, preferably with overall uncertainty expressed in terms of pressure not exceeding 0.03 % for given temperature and density.
- Sound speeds above 473 K in the vapor, liquid, and supercritical regions, preferably of similar accuracy to the measurements reported in [4].
- Heat capacities (either isobaric or isochoric), especially in the liquid (with uncertainty of 0.1 % or better) and near the critical point.
- Data for the vapor-liquid surface tension, especially at temperatures between 350 K and 550 K, with uncertainty less than 0.2 mN/m [5].

Needs for Theory and Modeling

- Data for the second and third virial coefficient, $B(T)$ and $C(T)$, would help the description of the vapor at low and medium pressures, including the metastable vapor. Outside a relatively narrow range of temperatures, these are difficult to measure accurately and the best data may be obtained from calculations using state-of-the-art intermolecular potentials. The work described in [6] provides some good values of $B(T)$, but more work on the pair potential, particularly on its flexibility and its uncertainty, is needed to determine the uncertainties of these values. The authors of [6] demonstrated a rigorous calculation of the third virial coefficient, but concluded that existing 3-body potentials for water are not good enough for quantitative prediction of $C(T)$. Therefore, improved 3-body potentials for water are needed.
- More accurate values for the ideal-gas heat capacity, which is fundamental to calculation of caloric properties, may be obtained from calculation of the partition function based on spectroscopic data supplemented by molecular modeling. This

has already been done for the most abundant water isotopologue $H_2{}^{16}O$ [7] and for the fully deuterated species [8], but this work must be extended to the other isotopologues that exist in ordinary water.

- Molecular simulation of liquid water in experimentally inaccessible states. While for the most part molecular simulation cannot match experimental accuracy, there are regions that are difficult or impossible to measure where simulations can guide the behavior of the equation of state. The metastable fluid inside the two-phase envelope is in this category, including where the water is stretched (under tension). Accurate volumetric properties, if possible including the isothermal compressibility, would be helpful, as would simulation that could locate the vapor-liquid spinodal. Ideally the simulations would cover a wide range of temperatures down to approximately the triple point. Simulations should be performed with physically realistic potentials (including multibody effects) and should include nuclear quantum effects (at least at low temperatures). They should also be performed at nearby well-measured conditions for validation. Studying finite-size effects and estimating uncertainties would be desirable. Simulation in the unstable region (inside the spinodal) is a more difficult challenge, but would be helpful to constrain the equation of state.
- Quantitative molecular simulation results for density (and possibly other properties such as sound speed) at high temperatures and pressures beyond conditions covered by experiments, validated against experiment in nearby regions where data exist. Temperatures above 800 K and pressures above 200 MPa would be of interest.
- Estimation of uncertainties of properties calculated from IAPWS-95 is somewhat *ad hoc*. It would be desirable to have a prescription for estimating the uncertainty of the equation of state in any calculated property for any pair of input variables. Realistic uncertainty estimates should incorporate to the extent possible uncertainties of input data, correlations among input data, theoretical constraints, and statistics of the fit such as parameter covariance.

References

[1] 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

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[4] C.-W. Lin and J.P.M. Trusler, The speed of sound and derived thermodynamic properties of pure water at temperatures between (253 and 473) K and at pressures up to 400 MPa, *J. Chem. Phys.* **136**, 094511 (2012).

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[8] I. Simkó, T. Furtenbacher, J. Hrubý, N.F. Zobov, O.L. Polyansky, J. Tennyson, R.R. Gamache, T. Szidarovszky, N. Dénes, and A.G. Császár, Recommended Ideal-Gas Thermochemical Functions for Heavy Water and its Substituent Isotopologues, *J. Phys. Chem. Ref. Data* **46**, 023104 (2017).

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