

## ***Interactive comment on “Development of thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography” by R. Feistel et al.***

R. Feistel et al.

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Referee #1 commented that

"However, the scope of this particular contribution seems rather limited. It does give an overview of the new seawater standard, but the (so far) unique material here simply 1. improves the definition of the ice-water-steam triple point, giving its value in quadruple precision and correcting the value of the 11th place of the  $g_{00}$  term of the Gibbs function for ice. 2. sets out quadruple precision numerical values for the properties of the reference states of pure water and of seawater. 3. summarizes a report (not referenced) of an IAPWS task group that concluded that the Helmholtz function for pure liquid water, strictly valid only above the freezing point of pure water, was in

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fact an adequate description of supercooled water below pure water freezing point (as is necessary to generate the Gibbs function for salty water, whose freezing point is depressed).

There is nothing wrong with the quality of the work described here, but I feel it is marginal whether this material merits publication in a separate contribution, or whether it would be better included in one of the more definitive papers in preparation. Certainly, if it is to remain a separate contribution, the title could be changed; the present title "Development of thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography" gives the impression of a much more substantial piece of work, and will be of no help to anybody looking for the specific points that are here."

Oceanographers are likely unaware of the effort IAPWS has spent on the development of the three potentials during the past two decades; our first aim was to explain the history and the reasons of this process in the form of a brief review paper that would appear in the literature commonly accessed by the oceanographic community. Combining the three potentials into a joint formulation was not a smooth and easy process as it may appear in retrospect; we explain problems we encountered and the solutions we found. We are not aware of any other publication that describes these problems or their solutions. We are convinced that the building-block concept we are proposing is the proper way to go with similar future tasks, e.g. for the description of conditions at the ocean-atmosphere interface. This paper is intended as a guideline for similar developments of standard formulations in connection with water (IAPWS-95), i.e. it is addressed to developers of such formulations as well as to their users.

A particularly difficult problem was the dynamic adjustment to the reference-state conditions recommended in IAPWS-95. At the end of our learning curve we came to the conclusion that dynamic adjustment is fine for a single potential, or to produce quadruple-precision reference values as we did during the development process, but static adjustments are necessary and sufficient to be provided to the final users if combinations of mutually consistent potentials are to be delivered.

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Finally, the shading of digits is an important output that tells the user how many digits of his/her double-precision implementation are likely free of numerical noise and comparable with results from other platforms. Results differing in the shaded range should not trigger any scientific dispute.

We understand the issue of mutual consistency and high-precision adjustment of free coefficients as a separate and rather enclosed problem on its own that deserves publication. Other papers should be enabled to just refer to these results rather than repeating and discussing them explicitly again.

Thanks for the technical corrections.

"p383 I11 Not clear what 657(10) means; does this mean that 7 is the last certain digit?"

This notation is explained on page 133 of the 2006 SI brochure "The International System of Units (SI)", [http://www.bipm.fr/utills/common/pdf/si\\_brochure\\_8\\_en.pdf](http://www.bipm.fr/utills/common/pdf/si_brochure_8_en.pdf) . A reference to this document is now included in the text.

Referee #2 has asked two questions:

"1) In section 4 the authors report that the potentials behave well in the metastable regimes. How was this tested? There is no mention to what datasets were used and how strict the test was."

As mentioned, Wagner and Pruß (2002) investigated this problem in detail. Additionally, special tests of the IAPWS-95 Helmholtz function were performed by the IAPWS taskgroup regarding the smooth displacement of the density maximum even below the freezing point, and of the significance of the highest powers of the expansion, which start to dominate a formula when the extrapolation error increases. In the revised version we have also added that recent density measurements below 0 °C at high pressures (Sotani et al. 2000, Asada et al. 2002) agree with IAPWS-95 within 0.05% over the oceanographic pressure range up to 100 MPa.

"2) The authors comment on the fact that different isotopic compositions affect the triple point temperature, and that isotopic fractionation in phase transition can actually lead to an ambiguous triple point. How is this physical problem translated in the mathematical model? Under what circumstances and for what type of applications does the different isotopic composition of seawater associated with different climates make a difference for its thermodynamic properties?"

The users of triple-point cells of metrological institutes and calibration laboratories dealing with the accuracy of the thermometers to realize the present temperature scale ITS-90 are the primary groups to which this point is addressed. Modern high-precision experiments require temperature stability in the range of microkelvins (e.g. Bettin & Toth 2006, Rudtsch 2008). The ice point of water relative to the triple point is known theoretically to this uncertainty (IAPWS 2006), i.e. better than the absolute ITS-90 temperature itself.

If the isotopes of water ( $^1\text{H}$ ,  $^2\text{D}$ ,  $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ) are explicitly considered, water is a mixture rather than a pure substance. Each water isotope as a pure substance has a slightly different chemical potential, and therefore a slightly different triple point. When the isotopes are mixed, the three phases liquid-vapor-solid of this water may coexist at slightly different temperatures and pressures in a "triple region"; where at each specific T and P the isotopic ratios within those phases take different values ("defractionate")

Referee #3 mentioned that

"Doubtless these are important improvements for anyone concerned with the physical properties of seawater. I found the writing rather dense, geared to the specialist, I suppose. I wondered how I could use the data in the tables to calculate, say, the saturation vapor pressure variation near the triple point. If I really needed to, I guess I would figure it out. Yet it would have been handy to have unpacked some of the dense prose."

The paper and its tables are mainly addressed to developers of such formulations

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rather than their users. The tables should provide accurate reference values for any future attempt of a similar kind, assuming that IAPWS-95 will remain the fundamental water standard for a considerable period of time. Provision of a primer on the use of the Gibbs function formulation is beyond the scope of this article but is adequately covered by the references given in the text.

#### References:

Asada, S., Sotani, T., Arabas, J., Kubota, H., Matsuo S., and Tanaka, Y.: Density of water at subzero temperature under high pressure: measurements and correlation, *J. Phys.: Condens. Matter*, 14, 11447-11452, 2002.

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