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THE INTERNATIONAL IAPWS STANDARD FOR THE THERMODYNAMIC PROPERTIES OF SEAWATER FOR DESALINATION PROCESSES

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Abstract

The development and operation of desalination plants require the knowledge of accurate thermodynamic properties of seawater and their fast calculation. Therefore, the International Association for the Properties of Water and Steam (IAPWS) adopted the "Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (IAPWS-2013) as an international standard for the calculation of the thermodynamic properties of seawater for industrial use. This standard contains an equation of state for the Gibbs free energy for seawater which consists of one part for pure liquid water and one part for dissolved sea salt. The water part is calculated from the "IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97) and the saline part from the "IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" (IAPWS-08). For seawater in contact with ice, the "Revised IAPWS Release on an Equation of State 2006 for H_2O ice Ih" (IAPWS-2006) is used.

The purpose of this paper is to introduce the new IAPWS industrial standard for the thermodynamic properties of seawater to the community of desalination plant developers and operators to enable more accurate and efficient calculations in their daily work.

The industrial formulation is valid for seawater with sea salt of the reference composition at temperatures from –12 °C to 80 °C, pressures from 0.3 kPa to 100 MPa, and salinities from 0 (pure water) to 120 g kg^{-1}, with some restrictions in certain regions.

All thermodynamic properties such as density, specific volume, specific enthalpy, specific isobaric heat capacity, and specific entropy, thermodynamic derivatives e. g. cubic isobaric expansion coefficient or isothermal compressibility can be calculated from this Gibbs free energy equation for seawater. In addition, boiling temperature, freezing temperature, osmotic pressure, and properties for brine-vapor mixtures and brine-ice mixtures are calculable.

When using the industrial formulation IAPWS-2013, the uncertainties of the calculated seawater properties are slightly greater than those of the scientific formulation IAPWS-08. The difference results from the use of IAPWS-IF97 in the former and the use of the scientific formulation IAPWS-95 in the latter for the pure-water part.

The computing speed of the industrial formulation IAPWS-2013 for seawater is increased in the order of 100 to 200 depending on the property function in comparison with the use of the scientific formulation IAPWS-08.

The industrial formulation IAPWS-2013 for seawater can be applied in calculations for analyzing, designing, simulating, operating, and optimizing desalination processes and for cooling processes with seawater in power plants.

I. INTRODUCTION

In 2008, IAPWS adopted the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater (IAPWS-08) [1], where the thermodynamic properties of seawater are calculated from an equation of state, consisting of a water part and a saline part. The water part is computed from the Helmholtz free energy equation of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (IAPWS-95) [2]. The saline part is formulated as a Gibbs free energy equation.

However, the iterative calculation of required properties from the IAPWS-95 Helmholtz free energy equation is computationally intensive, making its use less desirable in applications where computational speed is important. In modeling industrial desalination and cooling processes, it is more reasonable to use the Gibbs free energy equation of Region 1 of the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (IAPWS-IF97) [3] for the water part of the seawater formulation instead of IAPWS-95. In addition, the IAPWS-IF97 Industrial Formulation is already being used by industry for calculating properties of pure steam and water for power plants and their components.

Therefore, the International Association for the Properties of Water and Steam (IAPWS) adopted the "Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (IAPWS-2013) [4] as an international standard for the calculation of the thermodynamic properties of seawater for industrial use.

II. THERMODYNAMIC PROPERTIES OF SEAWATER

The IAPWS-2013 equation of state for the liquid mixture "seawater" [4, 5] is in the form of the specific Gibbs free energy as a function of pressure *p*, temperature *T*, and salinity *S*, and reads

$$g(p,T,S) = g^{\mathrm{W}}(p,T) + g^{\mathrm{S}}(p,T,S)\ . \qquad (1)$$

The water part $g^{\mathrm{W}}(p,T)$ is computed from the industrial formulation IAPWS-IF97 [3], and the saline part $g^{\mathrm{S}}(p,T,S)$ from the IAPWS-08 seawater formulation [1]. Salinity *S* is the mass fraction of sea salt in seawater. The composition of sea salt is assumed to be the Reference Composition of Standard Seawater. All thermodynamic properties and derivatives can be calculated from Eq. (1) by using the appropriate combinations of the Gibbs free energy equation and its derivatives with respect to *p*, *T*, and *S*.

III. COLLIGATIVE PROPERTIES

3.1 Phase Equilibrium between Seawater and Water Vapor

For computation of the equilibrium between seawater and water vapor, the required thermodynamic condition is the equality of the chemical potential of H_2O in seawater μ_{W} with the specific Gibbs

energy of water vapor g^{vap}. Here, chemical potentials are expressed on a mass basis, which is the usual (molar) chemical potential divided by molar mass.
For the phase equilibrium between seawater and water vapor, the following condition must be fulfilled:

$$\mu_{\text{W}}(p,T,S) = g^{\text{vap}}(p,T), \quad (2)$$

where $g^{\text{vap}}(p,T)$ is calculated from the Gibbs free energy equation of the IAPWS-IF97 region 2 [3]. Using Eq. (2), the boiling temperature can be calculated by iteration from pressure p and salinity S, or boiling pressure from temperature T and salinity S, or brine salinity from p and T.

3.2 Phase Equilibrium between Seawater and Ice

For the phase equilibrium between seawater and ice Ih, the following condition has to be fulfilled:

$$\mu_{\text{W}}(p,T,S) = g^{\text{Ih}}(p,T), \quad (3)$$

with the Gibbs free energy of ice Ih $g^{\text{Ih}}(p,T)$ calculated from the Gibbs free energy equation of the corresponding IAPWS Release [6].
Using Eq. (3), the freezing temperature can be calculated by iteration from pressure p and salinity S or the freezing pressure from T and S, or brine salinity from p and T.

3.3 Osmotic Pressure

The osmotic pressure p_{osm} is computed by iteration for pressure p, temperature T, and salinity S from the condition

$$\mu_{\text{W}}\left[(p + p_{\text{osm}}),T,S\right] = g^{\text{W}}(p,T). \quad (4)$$

IV. RANGE OF VALIDITY AND UNCERTAINTY

The equation of state, Eq. (1), is valid for Standard Seawater with sea salt of the Reference Composition inside the following pressure, temperature, and salinity ranges

$$0.3\ \text{kPa} \le p \le 100\ \text{MPa},\ \ -12\ ^\circ\text{C} \le T \le 80\ ^\circ\text{C},\ \text{and}\ \ 0 \le S \le 120\ \text{g kg}^{-1}$$

with some restrictions, described in [4].

V. UNCERTAINTY

The deviations between properties calculated from the industrial seawater formulation IAPWS-2013 and calculated from the scientific formulation IAPWS-08 cause by the use of IAPWS-IF97 instead of IAPWS-95 are small compared to the uncertainties in IAPWS-08. Therefore, the total uncertainties of the industrial seawater formulation IAPWS-2013 are generally equivalent to those of the IAPWS-08 formulation.

VI. COMPUTING TIME FOR THE IAPWS SEAWATER FUNCTIONS

One important reason to use IAPWS-IF97 instead of IAPWS-95 for calculating the water part of the IAPWS seawater functions is the computing-speed difference between these two standards. The relations of the computing speed of the seawater functions of the 2008 IAPWS seawater formulation [1] (which uses IAPWS-95) in comparison with the industrial formulation for seawater given herein (using IAPWS-IF97) were investigated. Improvements in speed by factors on the order of 100 or 200 were reported. While the observed improvement will depend on the efficiency with which IAPWS-95 is programmed (and also on details of the machine and compiler used), the use of IAPWS-IF97 clearly produces a significant reduction in computing time.

VII. SUMMARY

In this paper, the industrial calculation of seawater properties was carried out using the algorithms of IAPWS-IF97 for pure water. This was a requirement by industry which routinely uses the industrial formulation IAPWS-IF97 for process calculations that are often demanding on computer time. The main advantage of using the algorithms of IAPWS-IF97 instead of IAPWS-95 is to avoid iterative calculations from the IAPWS-95 Helmholtz free energy equation which is computationally intensive and therefore less desirable in applications where processing speed is important.
To verify the accuracy of the industrial formulation of seawater, extensive comparison calculations were carried out for the difference between the algorithms of the industrial formulation IAPWS-2013 for seawater and the scientific formulation IAPWS-08. The results showed that the differences between the two seawater formulations are very small. Consequently, the accuracy of this industrial formulation is nearly the same as that of IAPWS-08. The range of validity of the industrial formulation of seawater is the same as given for IAPWS-08. The computing-time comparison presented here leads to the conclusion that the calculation of seawater properties using the industrial seawater formulation is approximately 200 times faster than calculation using the original IAPWS-08 Formulation. In conclusion, the industrial formulation presented here is recommended for use in desalination or cooling processes.

VIII. REFERENCES

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