ICRN 16

IAPWS Certified Research Need – ICRN

Thermophysical Properties of Seawater

The IAPWS Working Group "Thermophysical Properties of Water and Steam" has examined the published work and experimental data available for description of seawater with natural composition of the dissolved salt, under the conditions appearing in the ocean and in technical systems like power stations or desalination plants.

The available information is not sufficiently accurate and comprehensive to permit:

(a) The construction of a comprehensive and accurate thermodynamic equation of state over the entire ranges of interest in oceanographic research, underwater technology and land-based industrial plants running on seawater

(b) The description of important transport properties of seawater like electrical conductivity, viscosity, diffusivity, or thermal conductivity over the entire ranges of interest

(c) The construction of a comprehensive and accurate optical equation of state over the entire ranges of interest required for fast and reliable in-situ sensors

(d) The description of solubility limits of its chemical components under different conditions of temperature, salinity and pressure

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

Issued by the
International Association for the Properties of
Water and Steam

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Background

While seawater is the most abundant liquid in the human environment, the quantitative knowledge of seawater properties is still very limited compared to, for instance, pure water. Ship traffic, tourism, fishery and fish breeding, underwater drilling and mining, onshore and offshore technical constructions for various purposes, the sea as a resource for the production of energy, freshwater, salt or hydrogen, and as a sink for anthropogenic CO_2, fertilisers or waste of any kind, and last not least the ocean as the main regulator of the global climate system, is all related to seawater. Their models or simulations require property data with increasing demand for accuracy and range of validity.

The description of seawater equilibrium properties, which is currently in use as the international standard for oceanography, is the 1980 International Equation of State of Seawater (EOS-80), released by the Joint Panel on Oceanographic Tables and Standards (JPOTS), published by Unesco (Fofonoff & Millard 1983). It is based on the temperature scale IPTS-68 and on the Practical Salinity Scale 1978, PSS-78 (Lewis & Perkin 1981). The salinity defined by PSS-78 is derived from the electrical conductivity of seawater and is expressed in dimensionless values, called the Practical Salinity, which approximately equals the absolute salinity in grams of sea salt with standard composition in 1 kilogram of seawater solution. Neither the conversion factor between Practical Salinity and absolute salinity, nor the chemical standard composition of sea salt are exactly defined by now. Rather, standard seawater samples taken from the surface of the North Atlantic are available from the International Association for the Physical Sciences of the Oceans (IAPSO).

EOS-80 is valid for temperatures between −2 and +40 °C, Practical Salinities between 2 and 42, and pressures between 0.1 and 100 MPa. The formulation consists actually of three independent correlation equations as functions of salinity, temperature and pressure, (i) for the density, (ii) for the speed of sound, and (iii) for the specific heat capacity at constant pressure. The set is extended (iv) by a correlation equation for the freezing temperature as a function of salinity and pressure, valid up to 5 MPa.

In 2006, as a successor of JPOTS, a Working Group 127 has been established by IAPSO and the Scientific Committee on Oceanic Research (SCOR). Its main objective is a recent evaluation of the current standards for seawater thermodynamics and, if necessary, the recommendation of improved formulations. Among the reasons for this revision process is the need for consistency between seawater properties and the more accurate recent international standards for temperature (ITS-90) and for properties of pure water (IAPWS-95).

This effort by IAPSO/SCOR is in accord with the current interest of IAPWS in an internationally recognised standard of seawater properties for scientific and industrial applications in general.

The Range of Properties Required

Ambient seawaters have salinities **between pure water and the saturation concentration** (typically more than 100 g/kg, depending on temperature and pressure), in particular in sea ice brines. Saturation is meant as the state where the first chemical sea salt component starts to precipitate or to degas from the solution. The temperature ranges **from the freezing**

point to the boiling point or, beyond the critical pressure, **to 680 K**, the currently highest temperature measured at a hydrothermal vent at 3000 m water depth. The pressure ranges **from 0 to 100 MPa**, corresponding to about 10 000 m water depth.

At atmospheric pressure, the range up to 120 °C and 70 g/kg is of particular interest for power station cooling and desalination.

These ranges include the conditions met in technical systems like desalination plants or the cooling systems of power stations.

The condition ranges given above include the critical point of water or seawater (Povodyrev et al. 1999, Sedlbauer & Wood 2004) and the triple point of water, i.e., the phase equilibria of seawater with ice or vapor.

In addition to the equilibrium properties of seawater required for the determination of a comprehensive equation of state like a Gibbs function (Feistel 2003), in particular the electrical conductivity and, with lower priority, the refractive index need to be determined for the construction and calibration of in-situ sensors to determine salinity, density or composition anomalies. Such sensors are inevitable for automatic observation tools.

Previous Work and Current Studies

Equilibrium properties of natural or artificial seawater outside the oceanographic standard range were considered in several studies and have briefly been reviewed by Feistel and Marion (2007) for high-salinity seawater at low temperatures and by Millero and Pierrot (2005) for higher temperatures. The available works mostly focus on properties like density, heat capacity, vapour pressure or osmotic coefficients at atmospheric pressure.

Much more and comprehensive studies are available for standard seawater inside the oceanographic standard range of salinity, temperature and pressure, Table 1.

The equilibrium properties of pure water in the *T-p* range of interest are well described by the IAPWS-95 Release of 1996.

Determinations of the **electrical conductivity** of seawater outside the oceanographic standard range were done by Poisson & Ghadoumi (1993). The conductivity of pure water in the *T-p* range of interest is described by the IAPWS Guideline of 1990.

The most relevant recent studies of the **refractive index** of seawater were published by Alford et al. (2006) and Millard & Seaver (1990). The refractivity of pure water in the *T-p* range of interest is described by the IAPWS Release of 1997.

Measurements of thermodynamic equilibrium properties or refractive index should preferably be performed relative to pure water, for **IAPSO standard seawater** and for **artificial seawater with Reference Composition** as specified in 2007 by the SCOR/IAPSO Working Group 127 (Millero et al. 2007). Measurements of electrical conductivity should preferably be performed relative to standard KCl solutions as described in the definitions of the Practical Salinity (Lewis and Perkin 1981) and the Reference-Composition Salinity (Millero et al. 2007).

Measurements of standard seawater at high pressures or at very low temperatures are almost completely missing, as are data about thermal expansion, compressibility, or sound speed. In Table 1, quantities and ranges in *S*, *t* and *p* are reported where sufficiently accurate experimental data are available. Outside the ranges given in Table 1, any

measurements of these quantities are needed for standard seawater in the ranges of properties required.

No experimental data of artificial seawater with Reference Composition are available yet. Measurements of the quantities given in Table 1 are needed everywhere in the ranges of properties required.

Table 1: List of quantities and property ranges for which accurate measurements are available for standard seawater. Ouside these ranges, measurements of the given quantities are needed.

Quantity	S g kg^{-1}	t °C	p MPa
Density	0 - 40	0 - 40	0.1 - 100
Heat capacity	0 - 120	0 - 200	0.1
Mixing enthalpy	0 - 110	0 - 30	0.1
Isothermal compressibility	none	none	none
Sound speed	33 - 37	0 - 5	0 - 100
Sound speed	29 - 43	0 - 30	0.1 - 5
Thermal expansion	10 - 30	−6 - 1	0.7 - 33
Freezing temperature	0 - 40	−2 - 0	0.1
Freezing temperature	27 - 35	−1 - −3	0.1 - 10
Freezing volume	none	none	none
Freezing enthalpy	none	none	none
Boiling temperature	0 - 70	60 - 120	0.1
Vapor pressure	20 - 40	25	-
Evaporation enthalpy	none	none	none
Saturation salinity	-	none	none
Electrical conductivity	0 - 40	0 - 40	0.1 - 100
Refractive index	0 - 40	0 - 30	0.1

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