

## **IAPWS Certified Research Need – ICRN**

### **Thermophysical Properties of Seawater**

The IAPWS Working Group “Thermophysical Properties of Water and Steam” and the IAPWS “Subcommittee on Seawater” have 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 such as electrical conductivity, viscosity, 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
- (e) The description of composition anomalies and pH values

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  
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Water and Steam**

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## Thermophysical Properties of Seawater

### 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<sub>2</sub>, fertilisers or waste of any kind, and last but 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 recent description of seawater equilibrium properties, which was endorsed by IAPWS in 2008 and UNESCO/IOC in 2009, is the core of the International Thermodynamic Equation of Seawater TEOS-10 (IOC et al., 2010). It is based on the temperature scale ITS-90 and the Reference-Composition Salinity Scale, RCSS (Millero et al., 2008) which is consistent with the Practical Salinity Scale 1978, PSS-78 (Lewis and Perkin, 1981). The salinity defined by RCSS can be estimated from the electrical conductivity of seawater and is expressed as a mass fraction which approximately equals the Absolute Salinity, i.e., the mass of sea salt with Reference Composition per mass of Standard Seawater solution. 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).

The current version of TEOS-10 is valid in certain subregions inside a  $S$ - $T$ - $p$  cuboid bounded by Reference-Composition Salinities between 0 and 120 g/kg, temperatures between -12 and +80 °C, and pressures between 0 and 100 MPa, as described in the IAPWS Release of 2008. The formulation is consistent with three thermodynamic potentials also endorsed by IAPWS, (i) the 2009 Release on fluid water, (ii) the 2009 Release on ice Ih, and (iii) the 2010 Guideline on humid air. From this combination, TEOS-10 provides the properties of the single phases as well as of phase equilibria between seawater and ice, water vapor or humid air.

### The Range of Properties Required

Ambient seawaters have salinities **between pure water and saturation** (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 the temperature of 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 pressures up to 10 MPa, temperatures up to 150 °C and salinities up to 100 g/kg are of particular interest for desalination and power station cooling.

The ranges of conditions given above include phase equilibrium states of seawater with ice, vapor or humid air, and in particular the critical point of water or seawater (Povodyrev et al. 1999, Sedlbauer and Wood 2004) and the triple point of water.

In addition to the equilibrium properties of seawater required for the determination of a comprehensive set of equations of state such as those in TEOS-10, other properties of

seawater are also of interest. In particular the viscosity, the electrical and the thermal conductivity and, with lower priority, the surface tension and 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 required for the development of highly desirable automatic observation tools. An unambiguous, full-range definition of the pH of seawater is required for the description of the acidification of oceans and estuaries by rising atmospheric CO<sub>2</sub> levels.

### Previous Work and Current Studies

**Equilibrium properties** of natural or artificial seawater outside the oceanographic standard range have been considered in several studies and were briefly 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 such as density, heat capacity, vapor 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, see Table 1.

The equilibrium properties of pure water in the  $T$ - $p$  range of interest are well described by the IAPWS-95 Revised Release of 2010.

Formulas for the **viscosity** of seawater are reviewed by Sharqawy et al. (2010). The viscosity of pure water is described in the IAPWS Release 2008.

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

Formulas for the **thermal conductivity** of seawater are reviewed by Sharqawy et al. (2010). The thermal conductivity of pure water is described in the IAPWS Revised Release 2008.

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

The **pH scales** for seawater are reviewed by Millero (2001). The ionization constant of pure water is available from the IAPWS Release 2007.

Formulas for the **surface tension** of seawater are reviewed by Sharqawy et al. (2010). The surface tension of pure water is described in the IAPWS Release 1994.

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 2008 by the SCOR/IAPSO Working Group 127 (Millero et al., 2008).

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), for IAPSO Standard Seawater and for artificial seawater with Reference-Composition (Millero et al., 2008) at elevated salinity, temperature or pressure, or should be **traceable to the SI** (Seitz et al., 2010).

Measurements of the density of Standard Seawater at high pressures or at very low temperatures are scarce (Safarov et al., 2009), 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. Additional measurements of these quantities are needed for Standard Seawater in the ranges of properties specified above, particularly outside the ranges given in Table 1.

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

Table 1: List of quantities and property ranges for which accurate measurements are available for Standard Seawater. Measurements of the given quantities are particularly needed outside of these ranges. Freezing volume and freezing enthalpy refer to the thermal expansion and the heat capacity, respectively, of a seawater-ice composite, and evaporation enthalpy to the heat capacity of a seawater-vapor composite.

Quantity	$S$ g kg <sup>-1</sup>	$t$ °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	-3 - -1	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	-
Osmotic pressure	none	none	-
Evaporation enthalpy	none	none	none
Saturation salinity	-	none	none
Surface tension	0 - 40	0 - 40	0.1
Viscosity	0 - 150	0 - 180	0.1 - 140
Electrical conductivity	0 - 40	0 - 40	0.1 - 100
Thermal conductivity	0 - 60	0 - 60	0.1 - 140
Refractive index	0 - 40	0 - 30	0.1

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