The IAPWS Industrial Formulation for the Thermodynamic Properties of Seawater

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Outline

The 3rd International Conference on Water Resource and Environment (WRE 2017), Qingdao, China, 26–29 June 2017

1. Introduction

- 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" as an international standard at its conference in London (2013).

- The following institutions and companies were involved in the development:
  - Zittau/Goerlitz University of Applied Sciences, Germany
  - Leibniz Institute for Baltic Sea Research, Rostock, Germany
  - Ruhr University of Bochum, Germany
  - K. Miyagawa, Tokyo, Japan
  - NIST, Boulder, USA
  - Queen Mary, University of London, England
  - Alstom Power, Baden, Switzerland
  - Moscow Power Engineering Insitute, Russia
  - Siemens Energy Sector, Erlangen, Germany
  - General Electric, Power & Water, Schenectady, USA

- In addition, there is a scientific standard for calculating thermodynamic properties of seawater, the IAPWS-2008 Formulation.
- The difference between both formulations is the calculation of the pure water part:

IAPWS-2008 Scientific Formulation → Scientific Formulation IAPWS-95

IAPWS Industrial Formulation 2013 → Industrial Formulation IAPWS-IF97

- The reasons for developing an industrial formulation were:

1. The IAPWS-95 is computationally intensive because it consists of an Helmholtz equation as a function of (T,ρ) and therefore all properties have to be calculated iteratively.
   → Computing speed is important for modeling and optimizing of processes, e.g., desalination processes.
2. The IAPWS-IF97 is used by industry for calculating properties of pure steam and water.
   → When using IAPWS-IF97 for seawater, the crossover of the calculations to pure water will be consistent.

2. Description of the IAPWS Industrial Formulation for Seawater
2.1 Fundamental Equation

Gibbs free energy equation for seawater

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

Water part calculated from IAPWS-IF97 region 1 equation

$$g^{\mathrm{W}} = g_1^{97}(p,T)$$

Saline part calculated from IAPWS Formulation 2008

$$g^{\mathrm{S}} = g^{08}(p,T,S)$$

The salinity S represents the mass fraction of sea salt in seawater

$$S = \frac{m_{\mathrm{S}}}{m}.$$

The composition of sea salt is based on the Reference Composition Scale of Standard Seawater.

⇨ All thermodynamic properties can be calculated from the fundamental equation $g(p,T,S)$ and its derivatives for p, T, and S.

Property	Calculation from $g(p,T,S)$
Specific volume	$v(p,T,S) = g_p$
Specific enthalpy	$h(p,T,S) = g - T\,g_T$
Specific entropy	$s(p,T,S) = -g_T$
Specific isobaric heat capacity	$c_p(p,T,S) = -T\,g_{TT}$
Cubic isobaric expansion coefficient	$\alpha_v(p,T,S) = \frac{g_{pT}}{g_p}$
Isothermal compressibility	$\kappa_T(p,T,S) = -\frac{g_{pp}}{g_p}$
Speed of sound	$w(p,T,S) = g_p \sqrt{\frac{g_{TT}}{\left(g_{pT}^2 - g_{pp}\,g_{TT}\right)}}$
Chemical potential of water	$\mu_W(p,T,S) = g - S\,g_S$
Osmotic coefficient	$\phi(p,T,S) = -\frac{g^S - S\,g_S}{b\,R_m\,T}$

$$g_T = \left(\frac{\partial g}{\partial T}\right)_{p,S} = \left(\frac{\partial g^W}{\partial T}\right)_p + \left(\frac{\partial g^S}{\partial T}\right)_{p,S}$$

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2.2 Phase Equilibrium between Seawater and Water Vapor

Phase equilibrium condition

$$\mu_W(p,T,S) = g^{vap}(p,T)$$

Chemical potential of water in seawater

Gibbs free energy of water vapor, calculated from IAPWS-IF97 region 2 equation

$$g^{vap}(p,T) = g_2^{97}(p,T)$$

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Calculation of the boiling temperature by iteration

$$T_b = T = f(p,S)$$

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Brine-vapor properties are calculated as follows:

Liquid seawater (brine) phase	$g(p,T_b,S)$
Vapor phase	$g_2^{97}(p,T_b)$

2.3 Further Properties

- Phase equilibrium between seawater and ice
- Properties of brine ice (sea ice)
- Triple-point temperatures and pressures
- Osmotic pressure

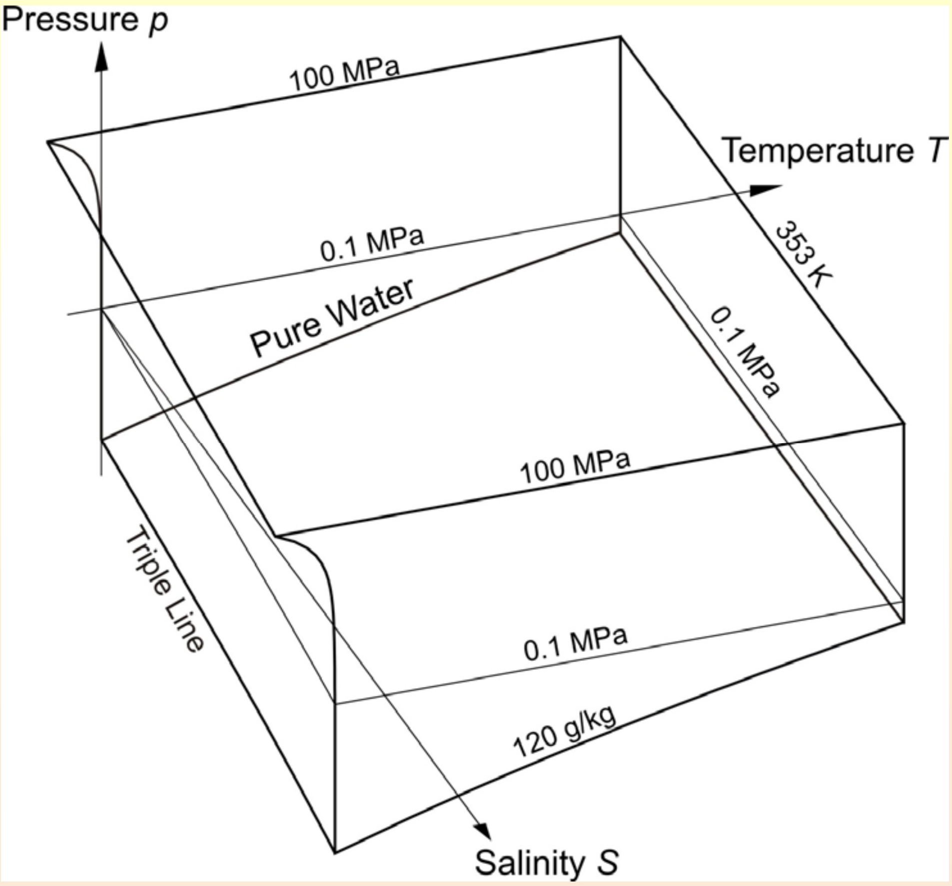
3. Range of Validity

Corresponding to the IAPWS 2008 Formulation

Pressure:	0.3 kPa … 100 MPa
Temperature:	261 K … 353 K
Salinity:	0 … 120 g / kg

with restrictions in certain regions according to IAPWS-2008

Illustrated Range of Validity of the IAPWS Industrial Formulation 2013 for Seawater



4. Uncertainty of the Industrial Formulation

Quantity	S interval kg kg^{-1}	T interval K	p interval MPa	u_{08}	Δ_{RMS}	u
$\left\|\frac{\Delta\rho}{\rho}\right\|$	0 - 0.04	273 - 313	0.1	4×10^{-6}	2.9×10^{-6}	5×10^{-6}
	0.04 - 0.05	288 - 303	0.1	1×10^{-5}	1.3×10^{-6}	1×10^{-5}
	0.005 - 0.04	273 - 313	10 - 100	2×10^{-5}	5.3×10^{-6}	2×10^{-5}
$\|\Delta\alpha_v\|$	0.01 - 0.03	267 - 274	0.7 - 33	6×10^{-7} K^{-1}	1×10^{-6} K^{-1}	1×10^{-6} K^{-1}
$\left\|\frac{\Delta w}{w}\right\|$	0.029 - 0.043	273 - 308	0.1 - 2	3×10^{-5}	8.2×10^{-4}	8.2×10^{-4}
	0.029 - 0.043	273 - 303	0.1 - 5	3×10^{-5}	6.4×10^{-4}	6.4×10^{-4}
$\left\|\frac{\Delta p^{vap}}{p^{vap}}\right\|$	0.02 - 0.12	293 - 353	0.002 - 0.05	1×10^{-3}	3.9×10^{-5}	1×10^{-3}
	0.018 - 0.04	298	0.003	2×10^{-4}	1.5×10^{-5}	2×10^{-4}
$\|\Delta T_f\|$	0.004 - 0.04	271 - 273	0.1	2 mK	0.014 mK	2 mK
$\|\Delta T_b\|$	0.006 - 0.07	333 - 353	0.02 - 0.05	2 mK	1.2 mK	2.3 mK
$\left\|\frac{\Delta\phi}{\phi}\right\|$	0.004 - 0.04	273	0.1	2×10^{-3}	- [a]	2×10^{-3}
	0.0017 - 0.038	298	0.1	2×10^{-3}	- [a]	2×10^{-3}
$\left\|\Delta_{T}^{S}\right\|$	0 - 0.04	273 - 313	0.1	0.5 J kg^{-1} K^{-1}	- [a]	0.5 J kg^{-1} K^{-1}
$\|\Delta c_p\|$	0 – 0.12	273 - 353	0.1	4 J kg^{-1} K^{-1}	1.3 J kg^{-1} K^{-1}	4.2 J kg^{-1} K^{-1}

⇨ The uncertainty of the Industrial Formulation IAPWS 2013 is comparable to that of the Scientific Formulation IAPWS 2008 and is sufficient for industrial use.

5. Computing Time Consumption

Comparison of the Computing time consumption by using the "Computing Time Ratio":

$$CTR = \frac{\text{computing time of IAPWS-2008}}{\text{computing time of the Industrial Formulation 2013}}$$

Property	**CTR**
Specific volume	243
Specific enthalpy	236
Specific entropy	220
Specific isobaric heat capacity	430
Chemical potential of water in seawater	134
Boiling temperature of seawater	206
Freezing temperature of seawater	32

The IAPWS Industrial Formulation 2013 for seawater is in average 200 times faster than the scientific Formulation IAPWS-2008

6. Property Library LibSeaWa for Seawater

Used Algorithms:
- IAPWS Industrial Formulation 2013
- Fichtner Handbook of Hömig (1978) for extending the range of state and for calculating transport properties

Range of Validity:
- Pressure 0.0023 … 100 MPa
- Temperature 273 … 493 K
- Salinity 0 … 200 g / kg

Ranges of State:
- Liquid seawater
- Brine vapor (mixture of saturated seawater and vapor)
- Vapor (pure water)

Property Functions: (40 functions)
- Thermodynamic properties
- Transport properties
- Backward functions
- Thermodynamic derivatives

Interface Programs:
- FluidEXL for Excel®
- FluidLAB for MATLAB®
- FluidMAT for Mathcad®
- FluidEES for Engineering Equation Solver (EES)®
- FluidVIEW for LabVIEW™
- FluidDYM for DYMOLA and SimulationX (Modelica)®

7. Summary

- There is a new international standard for calculating the thermodynamic properties of seawater for modeling processes using seawater, e.g., desalination processes: "IAPWS Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (IAPWS 2013).

  Available at: www.iapws.org, under "Releases and Guidelines"

- The paper "The IAPWS Industrial Formulation for the Thermodynamic Properties of Seawater" has been published: *Desalination and Water Treatment* **55**, 1177-1199 (2015).

- For calculating seawater properties, the property library LibSeaWa can be used in Excel, MATLAB, Mathcad, EES, LabVIEW, DYMOLA and SimulationX.

  More information at: www.thermodynamics-zittau.de, under "Property Libraries"

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This presentation is available at: www.thermodynamics-zittau.de, under "News"