IDA WORLD CONGRESS 2015

DESALINATION & WATER REUSE

Renewable Water Resources to Meet Global Needs

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

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15WC: 51533

The IAPWS Industrial Formulation for the Thermodynamic Properties of Seawater for Calculating Desalination Processes

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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 in 2013.
- The following institutions and companies were involved in the development: Zittau/Goerlitz University of Applied Sciences, Zittau, Germany; Baltic Sea Research Institute, Warnemuende, Germany; Ruhr-University of Bochum, Bochum, Germany; K. Miyagawa, Tokyo, Japan; NIST, Boulder, USA; Queen Mary, University of London, England; Alstom Power, Baden, Switzerland; Moscow Power Engineering Institute, Russia; Siemens Energy Sector, Erlangen, Germany; General Electric, Power & Water, Schenectady, USA

Initial Situation: The IAPWS Formulation 2008

"Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater"

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

↑ Water part calculated from IAPWS-95 Helmholtz free energy equation $f^{95}(T,v)$

↑ Saline part

$$g^{\mathrm{W}}(p,T) = f^{95}(T,v) - v \cdot \left[\frac{\partial f^{95}(T,v)}{\partial v}\right]_T$$

where v is calculated from $p = -\left[\frac{\partial f^{95}(T,v)}{\partial v}\right]_T$ by iteration

⇨ Industry is interested in calculating the water part from IAPWS-IF97 because of the consistency with other calculations and computing speed.

- 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	IAPWS Industrial Formulation 2013
↓	↓
Scientific Formulation IAPWS-95	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 desalination and cooling 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	$\mu_{\mathrm{W}}(p,T,S) = g - S\,g_S$
Osmotic coefficient	$\phi(p,T,S) = -\frac{g^{\mathrm{S}} - S\,g_S}{b\,R_{\mathrm{m}}\,T}$

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

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

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

⇩

Calculation of the boiling temperature by iteration

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

⇩

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 Properties of Brine-Vapor Mixture

Equation for the mixture of brine with water vapor

$$g^{BV}(p,T,S) = (1-x)\,g(p,T,S_b) + x\,g^{vap}(p,T)$$

Brine part calculated from Gibbs free energy equation for seawater

$$g(p,T,S_b) = g^W(p,T) + g^S(p,T,S_b)$$

Water vapor part calculated from IAPWS-IF97 region 2 equation

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

and mass fraction of water vapor in the seawater mixture (vapor fraction)

$$x = 1 - \frac{S}{S_b(p,T)}$$ with boiling-brine salinity $S_b = S_b(p,T)$

⇩

Calculation of brine-vapor properties e.g.: specific enthalpy

$$h^{BV}(p,T,S) = (1-x)\,h(p,T,S_b) + x\,h^{vap}(p,T)$$

2.4 Further Properties

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

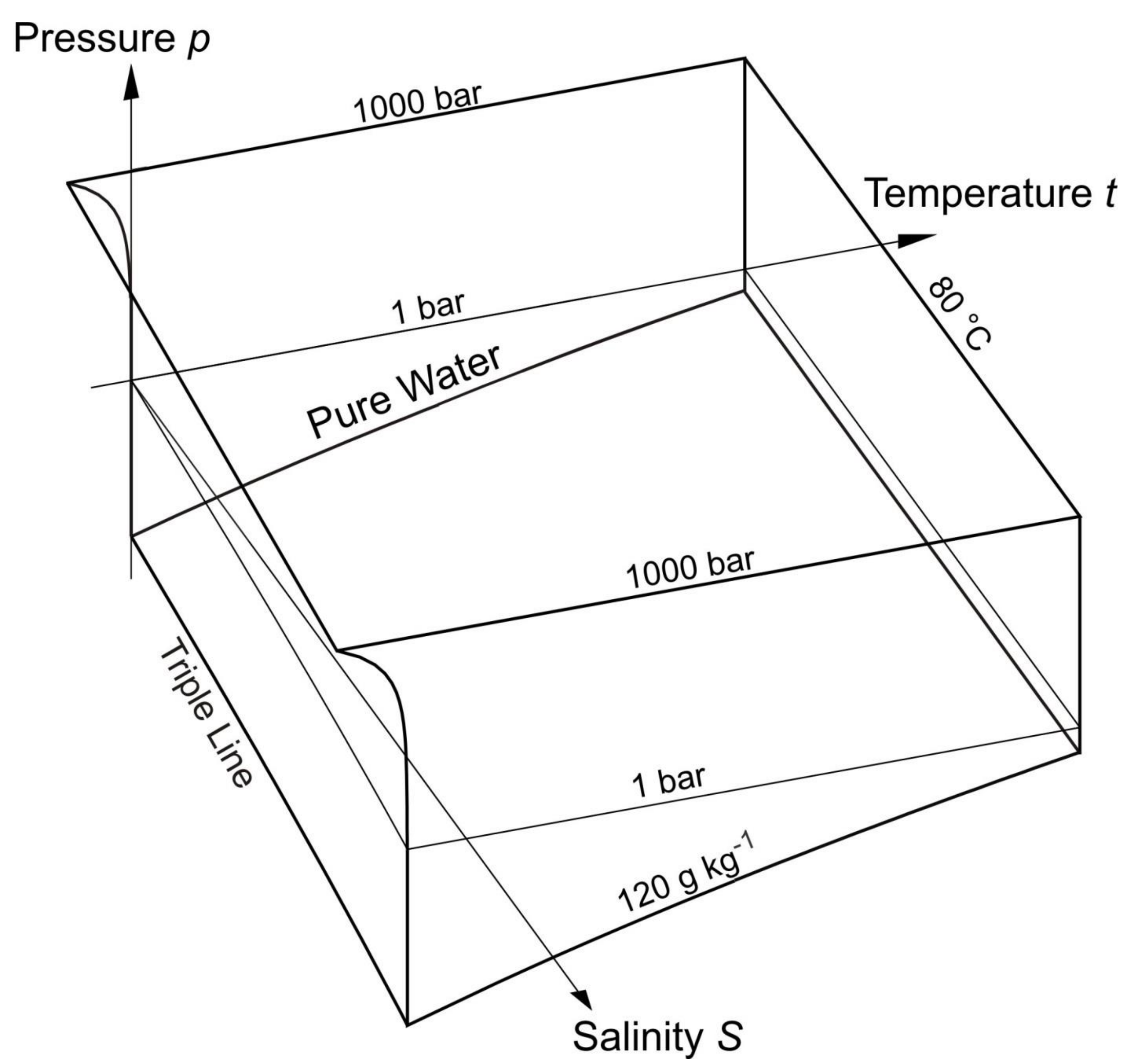
3. Range of Validity

Corresponding to the IAPWS 2008 Scientific Formulation

Pressure:	3 mbar … 1,000 bar
Temperature:	-12°C … 80°C
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

Report of K. Miyagawa, (2008), and an Update (2013)

- Comparison calculations were carried out regarding the difference between IAPWS-95 and IAPWS-IF97

U Uncertainty of Industrial Formulation	=	U_{08} Uncertainty of IAPWS-2008	+	Δ_{RMS} Difference between AN5 (IAPWS-IF97) and IAPWS-2008 (IAPWS-95)

Determination of the uncertainty of a certain property

$$u = \sqrt{u_{08}^2 + \Delta_{RMS}^2}$$

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	0.1 - 10	1×10^{-5}	2.6×10^{-6}	1×10^{-5}
	0.005 - 0.04	273 - 313	10 - 100	2×10^{-5}	5.3×10^{-6}	2×10^{-5}
	0.04 - 0.12	293 - 313	0.1	3×10^{-4}	4.2×10^{-6}	3×10^{-4}
	0 - 0.04	313 - 333	0.1	4×10^{-4}	1.3×10^{-5}	4×10^{-4}
	0.04 - 0.08	313 - 333	0.1	9×10^{-4}	1.3×10^{-5}	9×10^{-4}
	0 - 0.04	333 - 353	0.1	1.4×10^{-3}	1.5×10^{-5}	1.4×10^{-3}
	0.08 - 0.12	313 - 333	0.1	3×10^{-3}	1.3×10^{-5}	3×10^{-3}
	0.04 - 0.08	333 - 353	0.1	4×10^{-3}	1.5×10^{-5}	4×10^{-3}
	0.08 - 0.12	333 - 353	0.1	1.3×10^{-2}	1.6×10^{-5}	1.3×10^{-2}
$\left\|\Delta\alpha_v\right\|$	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}
	0.033 - 0.037	273 - 278	0.1 - 100	5×10^{-5}	1.8×10^{-4}	1.8×10^{-4}

Uncertainty of the Industrial Formulation (continued)

Quantity	S interval kg kg^{-1}	T interval K	p interval MPa	u_{08}	Δ_{RMS}	u
$\left\|\frac{\Delta p^{vap}}{p^{vap}}\right\|$	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}
$\left\|\Delta T_f\right\|$	0.004 - 0.04	271 - 273	0.1	2 mK	0.014 mK	2 mK
$\left\|\Delta T_b\right\|$	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}
	0.01 - 0.12	273 - 278	0.1	3×10^{-3}	- [a]	3×10^{-3}
$\left\|\Delta c_p^S\right\|$	0 - 0.04	273 - 313	0.1	0.5 J kg^{-1} K^{-1}	- [a]	0.5 J kg^{-1} K^{-1}
$\left\|\Delta c_p\right\|$	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":

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

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

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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 Hoemig (1978) for extending the range of state and for calculating transport properties

Range of Validity:
- Pressure 0.0023 … 100 MPa
- Temperature 0 … 220 °C
- 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 desalination and cooling 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"

- 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"