The IAPWS Industrial Formulation for the Thermodynamic Properties of Seawater

H.-J. Kretzschmar (Zittau, Germany), R. Feistel (Warnemuende, Germany), W. Wagner (Bochum, Germany),
K. Miyagawa (Tokyo, Japan), A.H. Harvey (Boulder, CO, USA), J.R. Cooper (London, UK),
M. Hiegemann (Baden, Switzerland), S. Herrmann (Zittau, Germany)

Contents

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1. Introduction

- IAPWS 2008 Release for calculating thermodynamic properties of seawater was adopted in 2008 → uses IAPWS-95 for calculation of the water part → very time consuming
- Industry need faster algorithms and consistensy with their water algorithms (IAPWS-IF97)
- A **Task Group** was set up consisting of:
  H.-J. Kretzschmar, R. Feistel, W. Wagner, K. Miyagawa, A.H. Harvey, J.R. Cooper, and S. Herrmann
- First investigations by K. Miyagawa “IAPWS-IF97 for the Water Part of the EOS for Seawater” (2008)
- Proposal for Draft Advisory Note No. 5 presented in Boulder 2012
- Contents of the proposal:
  - Based on IAPWS 2008 Formulation for seawater properties
  - Replacement of the algorithms of IAPWS-95 with IAPWS-IF97 for calculating the properties of the water part in the advisory note
- Decision in Boulder regarding the members of the **Evaluation Task Group**:
  I. Weber, A. Singh, M. Hiegemann, F. Blangetti, K. Orlov

⇨ Advisory Note No. 5 was finalized, evaluated, and adopted by IAPWS as an industrial standard on Sunday.

2. Description of the 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

where 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 $g(p,T,S)$.

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	$\alpha_V(p,T,S) = \dfrac{g_{pT}}{g_p}$
Isothermal compressibility	$\kappa_T(p,T,S) = -\dfrac{g_{pp}}{g_p}$
Speed of sound	$w(p,T,S) = g_p \sqrt{\dfrac{g_{TT}}{\left(g_{pT}^2 - g_{pp}\,g_{TT}\right)}}$
Chemical potential of water	$\mu_W(p,T,S) = g - S\,g_S$
Osmotic coefficient	$\phi(p,T,S) = -\dfrac{g^S - S\,g_S}{b\,R_m\,T}$

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

2.2 Phase Equilibrium between Seawater and Water Vapor

Phase equilibrium condition

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

Chemical potential
of water in seawater

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

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

⇩

Calculation of the boiling temperature by iteration

$$T_b = \mathrm{f}(p,S)$$

⇩

At an equilibrium state, properties are calculated:

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

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 … 0.12 kg kg^{-1}

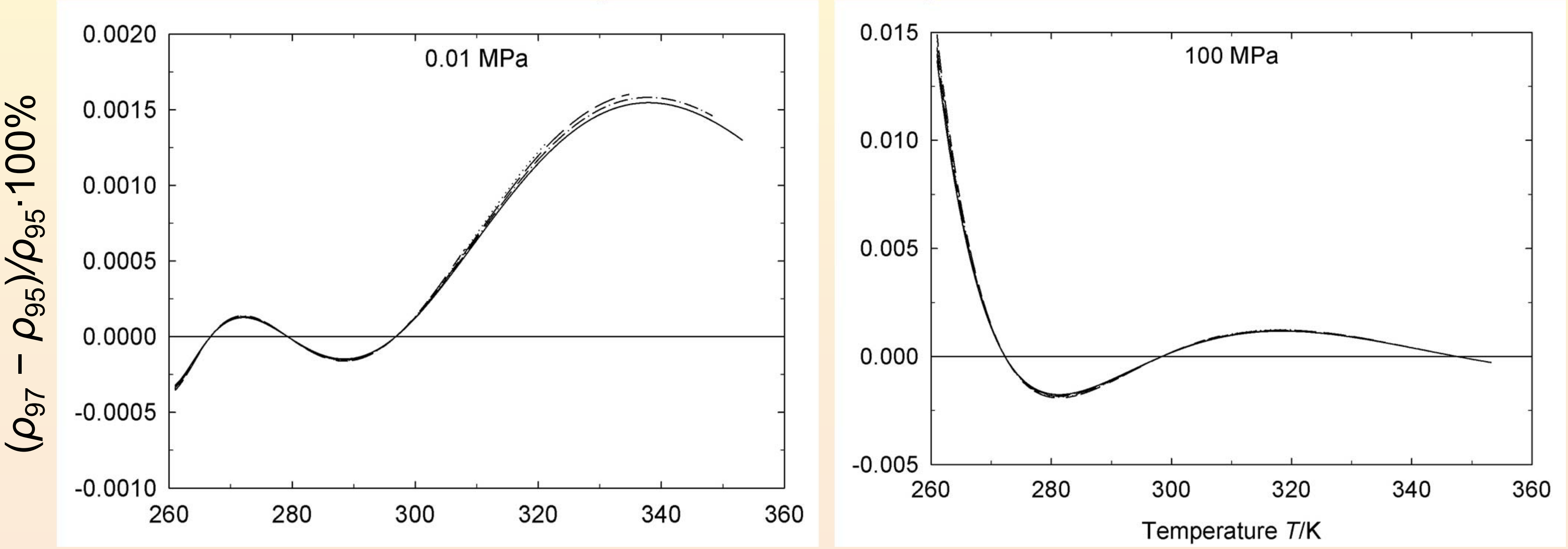
with restrictions in certain regions according to IAPWS-2008

4. Uncertainty

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

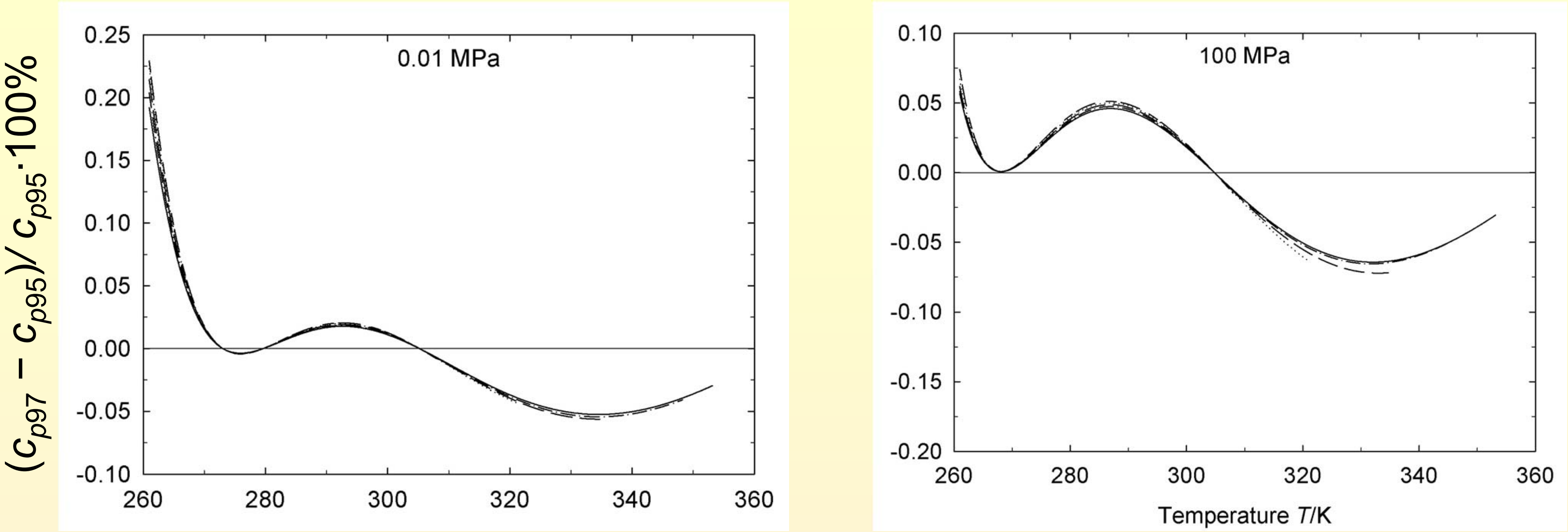
- Differences between IAPWS-2008 (IAPWS-95) and this work (IAPWS-IF97)
- Properties under investigation:
  density, specific isobaric heat capacity, and speed of sound
- Deviation plots were generated for eight different pressures between 0.01 MPa and 100 MPa, each at temperatures from 261 K to 353 K and for five different Absolute Salinities including pure water at 0, 0.03, 0.06, 0.09, and 0.12 kg/kg

Comparison of density values

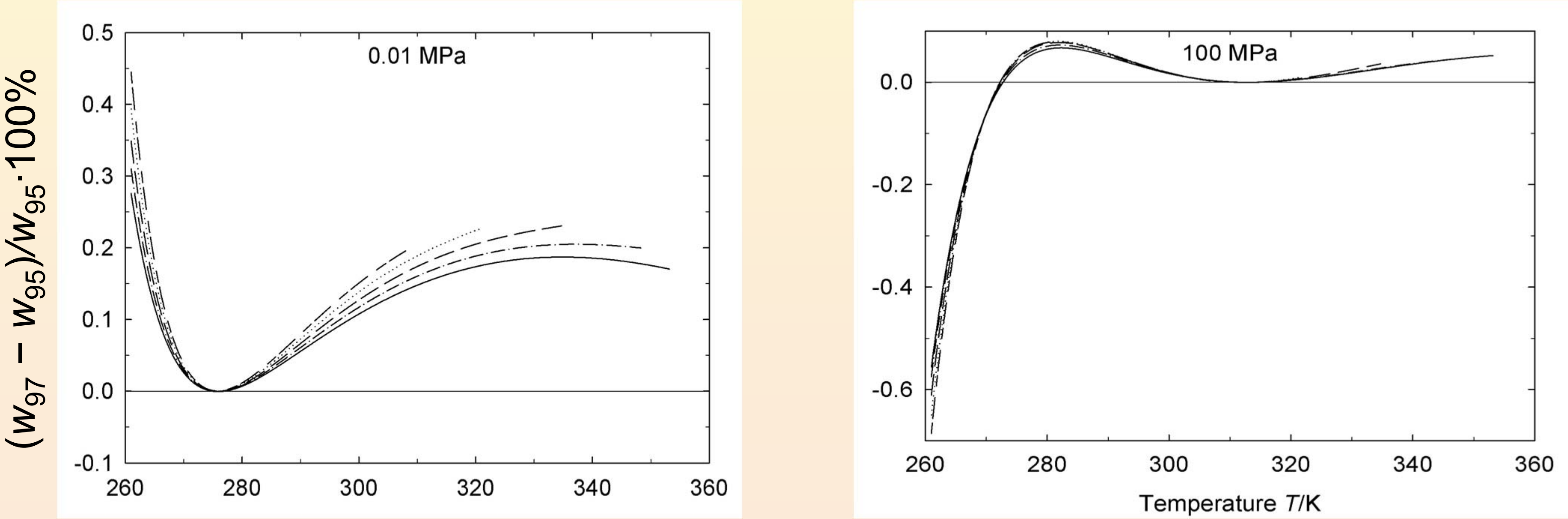


——, S = 0.00; ·····, S = 0.03; – – –, S = 0.06; –··–··–, S = 0.09; — —, S = 0.12

Comparison of isobaric heat capacity values

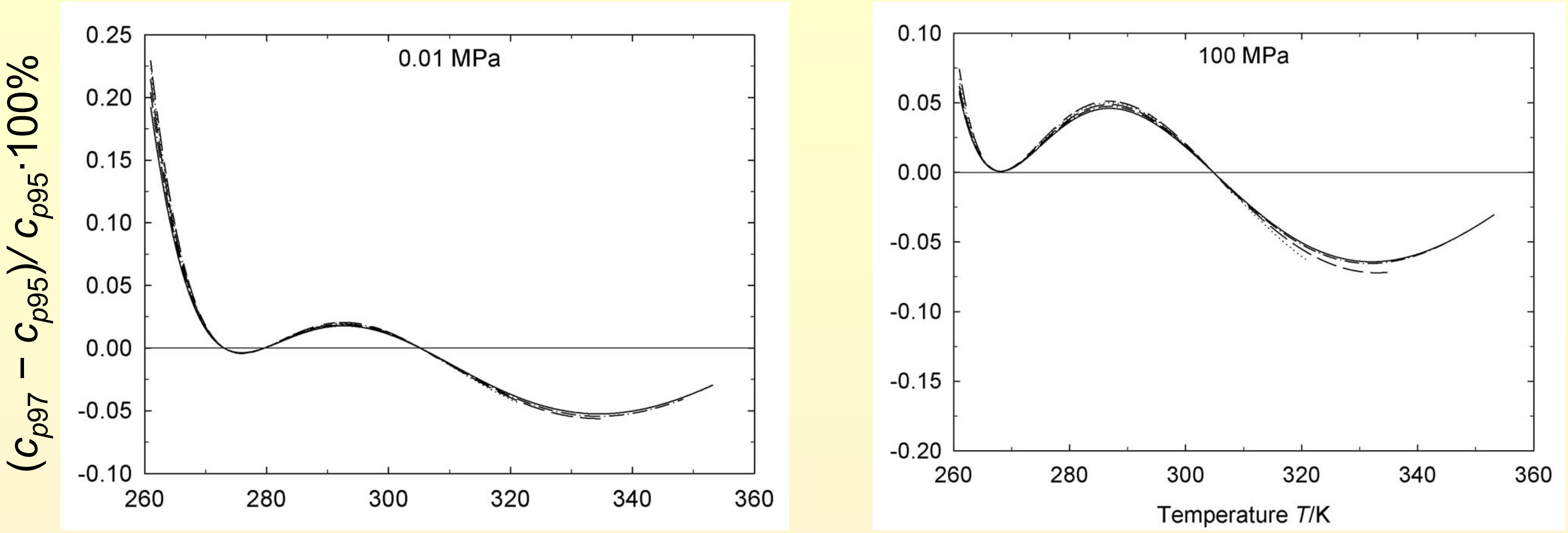


Comparison of speed of sound values



——, S = 0.00; ·····, S = 0.03; – – –, S = 0.06; –··–··–, S = 0.09; — —, S = 0.12

Comparison of isobaric heat capacity values



Results for uncertainty of properties, calculated using Advisory Note No. 5:

- No change of property values with varying **salinity**
- **Density**: negligible differences between IAPWS-2008 (IAPWS-95) and Advisory Note No. 5 (IAPWS-IF97) in the range of validity of IAPWS-IF97
- **Speed of sound** and **isobaric heat capacity**: small increase of uncertainty using IAPWS-IF97

5. Computing Time Comparison

Test report of K. Miyagawa → Computing time ratio of a quantity

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

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 industrial formulation for seawater is in average 200 times faster than IAPWS-2008

6. Summary

- Industrial Formulation IAPWS-IF97 replaces Scientific Formulation IAPWS-95 for calculating the water part in the algorithms of Advisory Note No. 5
- The range of validity of AN5 is as of IAPWS 2008 Release
- Uncertainties according to the difference between IAPWS-IF97 and IAPWS-95
- Computing time decrease by about 200 times

The Industrial Formulation for Seawater was adopted by IAPWS as an international standard here on Sunday.

Related paper was prepared and will be submitted to the journal *Desalination* soon

The IAPWS Industrial Formulation for the Thermodynamic Properties of Seawater

Hans-Joachim Kretzschmar, Rainer Feistel, Wolfgang Wagner, Kiyoshi Miyagawa,
Allan H. Harvey, Jeff R. Cooper, Michael Hiegemann, Francisco L. Blangetti,
Konstantin A. Orlov, Ingo Weber, Anurag Singh, Sebastian Herrmann

The IAPWS Formulation 2008

Initial Situation

“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.

2.4 Properties of Brine-Vapor Mixture

Equation for the mixture of brine with water vapor

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

Brine part calculated from Gibbs free energy equation for seawater

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

Water vapor part calculated from IAPWS-IF97 region 2 equation

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

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

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

⇩

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

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

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

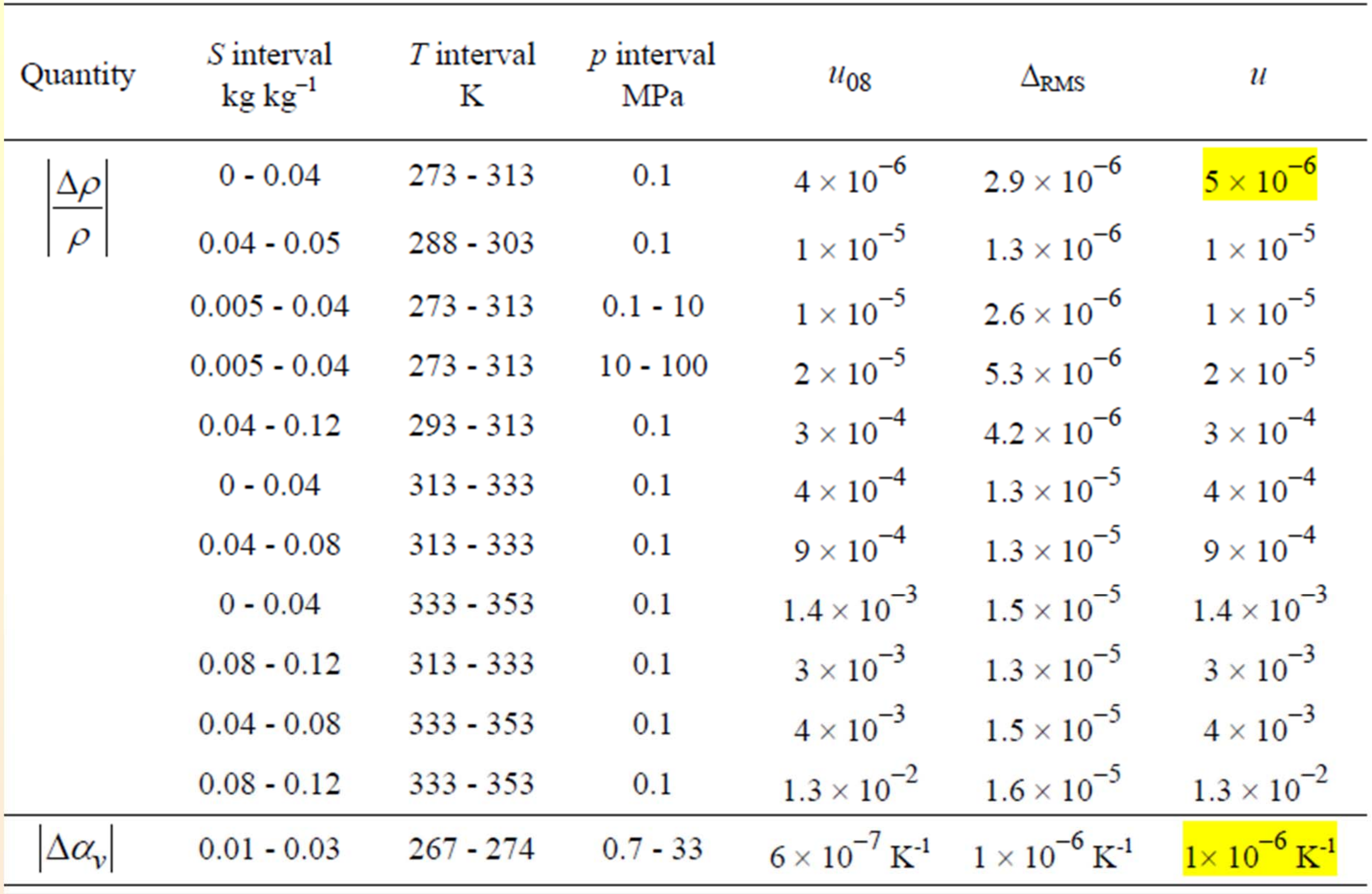
+

Δ_{RMS}
Difference between
AN5 (IAPWS-IF97)
and
IAPWS-2008
(IAPWS-95)

Determination of the uncertainty of a certain property

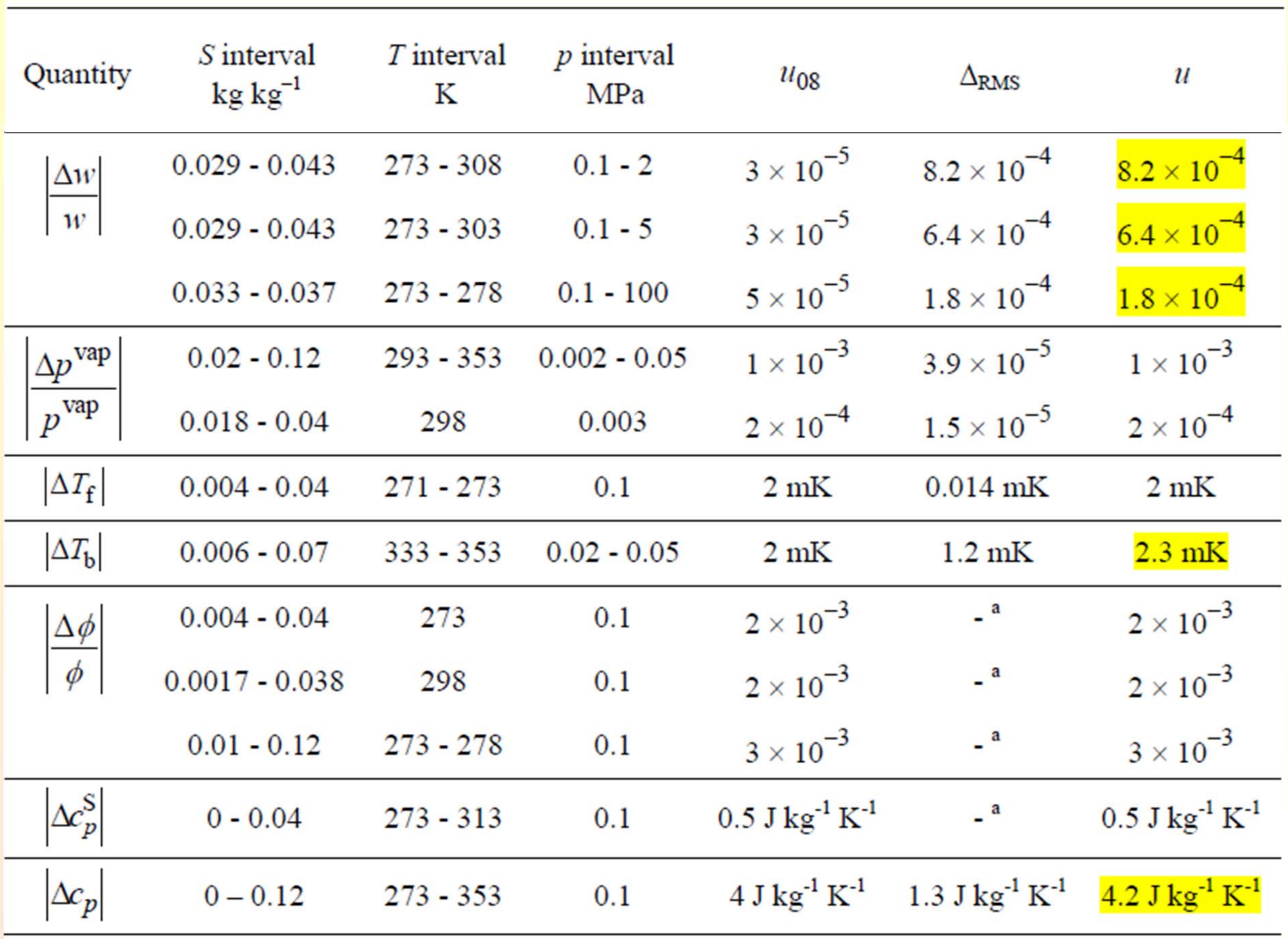
$$u = \sqrt{u_{08}^{2} + \Delta_{\mathrm{RMS}}^{2}}$$

Uncertainty I



Quantity	S interval kg kg^{-1}	T interval K	p interval MPa	u_{08}	Δ_{RMS}	u
$\left\|\dfrac{\Delta\rho}{\rho}\right\|$	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}

Uncertainty II



Quantity	S interval kg kg^{-1}	T interval K	p interval MPa	u_{08}	Δ_{RMS}	u
$\left\lvert\frac{\Delta w}{w}\right\rvert$	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}
$\left\lvert\frac{\Delta p^{\text{vap}}}{p^{\text{vap}}}\right\rvert$	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}
$\lvert\Delta T_{\text{f}}\rvert$	0.004 - 0.04	271 - 273	0.1	2 mK	0.014 mK	2 mK
$\lvert\Delta T_{\text{b}}\rvert$	0.006 - 0.07	333 - 353	0.02 - 0.05	2 mK	1.2 mK	2.3 mK
$\left\lvert\frac{\Delta \phi}{\phi}\right\rvert$	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}
$\lvert\Delta c_p^{\text{S}}\rvert$	0 - 0.04	273 - 313	0.1	0.5 J kg^{-1} K^{-1}	-[a]	0.5 J kg^{-1} K^{-1}
$\lvert\Delta c_p\rvert$	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}