

Thermodynamic Properties of Seawater, Ice and Humid Air: TEOS-10, Before and Beyond



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An unpublished lecture by Heinrich Hertz: “On the energy balance of the Earth”

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(Received 26 August 1996; accepted 6 September 1996)

This paper presents a recently discovered and newly translated manuscript of a lecture by Heinrich Rudolf Hertz, long famous for his 1888 discovery of long-wavelength electromagnetic waves. Hertz delivered this address on 20 April 1885 as his inaugural lecture to the faculty at the Technische Hochschule in Karlsruhe (now the Universität Karlsruhe), where he was to make his most important contributions to physics. Although written over 110 years ago, this historical document records both Hertz’s insightful view of the Earth’s energy situation at that time and his remarkably good order-of-magnitude estimates of the energy sources then known to be available to the Earth.

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INTRODUCTION

A brief history of the manuscript translated below may serve as a useful introduction to this lecture by Heinrich Rudolf Hertz (1857–1894). Hertz mailed the 50-page, hand-

written manuscript of his 20 April 1885 inaugural lecture at Karlsruhe to his father in Hamburg on 7 May 1885. Some years later his father presumably gave it to Heinrich’s brother, Rudolf, who in turn bequeathed it to his daughter,

The greater portion of the Earth’s surface is indeed covered with water, which evaporates under the influence of the incident solar radiation.

Every year, we may assume that on the average a water layer a meter high over the entire Earth is converted into water-vapor.

*This amount of energy serves as the heat source for a gigantic **steam engine**.*

Heinrich Hertz, 1885

Example 1:

Global Ocean Warming:

Observed and simulated full-depth ocean heat-content changes for 1970–2005

Lijing Cheng¹, Kevin E. Trenberth², Matthew D. Palmer³, Jiang Zhu¹, and John P. Abraham⁴

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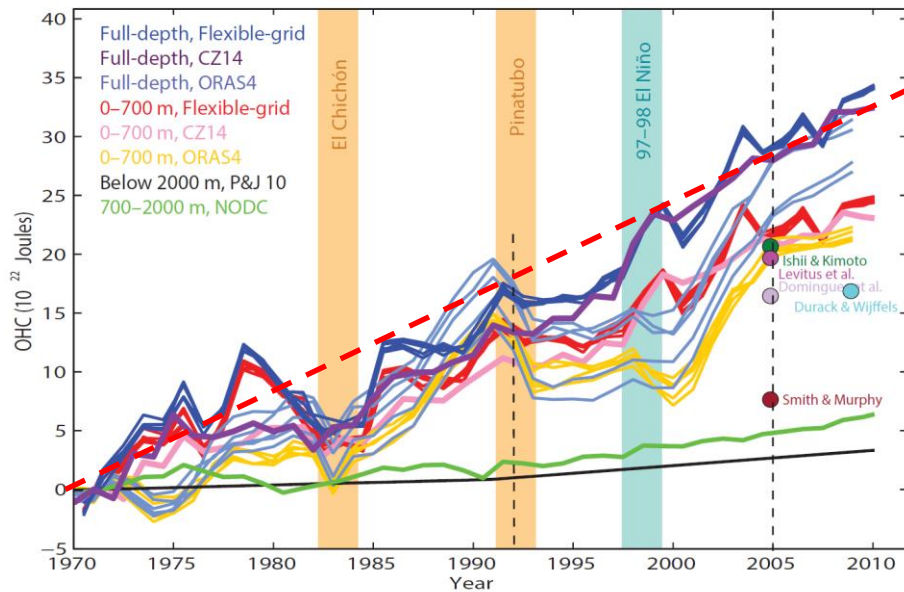


Figure 2. Observational ocean heat content from 1970 to 2010. The 0–700m OHC is shown in red (flexible-grid method), pink (CZ14 method), and yellow (ORAS4). Five adjusted OHCs presented in Durack et al. (2014) are shown as dots, which are the OHC changes per 35 years. The 700–2000m OHC is sourced from NODC in green, and abyssal (2000 m–bottom) OHC is from Purkey and Johnson (2010) and shown in black (the warming rate within 1970–1991 is scaled to 3 times the linear trend in Purkey and Johnson, 2010). Full-depth OHC time series are also presented in blue (flexible-grid method), dark purple (CZ14 method), and light blue (ORAS4). All of the time series are referred to a baseline OHC within the 3-year period: 1969–1971. The vertical colored bars are 2-year intervals, starting when the event (volcano or El Niño) began.

Heating Rate Estimate:

$$P = 30 \times 10^{22} \text{ J} / 35 \text{ yr} = 272 \text{ TW}$$

per Ocean Surface Area:

$$P / A_W = 0.75 \text{ W m}^{-2}$$

per Global Surface Area:

$$P / A = 0.54 \text{ W m}^{-2}$$



Example 2:

AMOC Reduction:

Impact of a 30 % reduction in Atlantic meridional overturning during 2009–2010

H. L. Bryden¹, B. A. King², G. D. McCarthy², and E. L. McDonagh²

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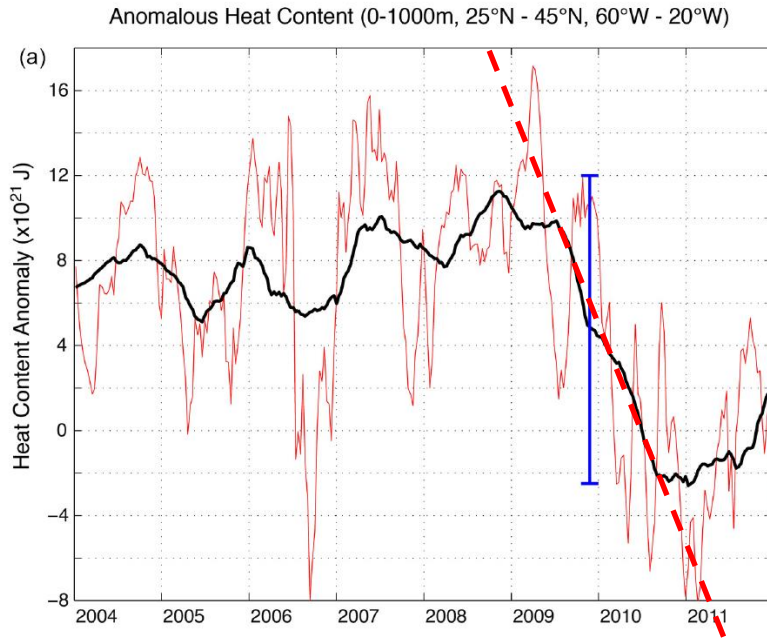


Figure 4. Anomalous heat content **(a)** north and **(b)** south of 25°N. Heat content anomaly is defined as the deviation in temperature from Hydrobase seasonal climatology multiplied by density and specific heat and integrated vertically from 0 to 1000m depth. Heat content anomaly is then integrated over 60 to 20°W and over latitude bands 25 to 45°N (north) and 10 to 25°N (south). The red curves represent 30-day average heat content and the black curves are 12-month running mean values. The blue bar represents a change in heat content of 14.5×10^{21} J.

Heat Flux Anomaly 2009 – 2010:

$$P = 12 \times 10^{21} \text{ J} / 1.2 \text{ yr} = 317 \text{ TW}$$

per Ocean Surface Area:

$$P / A_W = 0.88 \text{ W m}^{-2}$$

per Global Surface Area:

$$P / A = 0.63 \text{ W m}^{-2}$$

H. Hertz: „1 m Water = Heat Source of the Gigantic Steam Engine“

$$P / A = 1 \text{ m} \times 1000 \text{ kg m}^{-3} \times 2\,500\,000 \text{ J kg}^{-1} / 1 \text{ yr} = 79 \text{ W m}^{-2}$$

per Global Surface Area: $P / A = 79 \text{ W m}^{-2}$

per Ocean Surface Area: $P / A_W = 112 \text{ W m}^{-2}$

Thermodynamic driving force for evaporation: $E = r \Delta \frac{\mu_W}{RT} \approx -r \ln (RH)$

Climatological average: $112 \text{ W m}^{-2} = -r \ln (80\%)$

Hypothetical change of RH by 1%: $118 \text{ W m}^{-2} = -r \ln (79\%)$

Heat flux of 1%rh per Ocean Surface Area: $\Delta P / A_W = 6 \text{ W m}^{-2}$

Heat flux of 1%rh per Global Surface Area: $\Delta P / A = 4 \text{ W m}^{-2}$

Changing global ocean surface RH by < 1% may turn the ocean cooling !

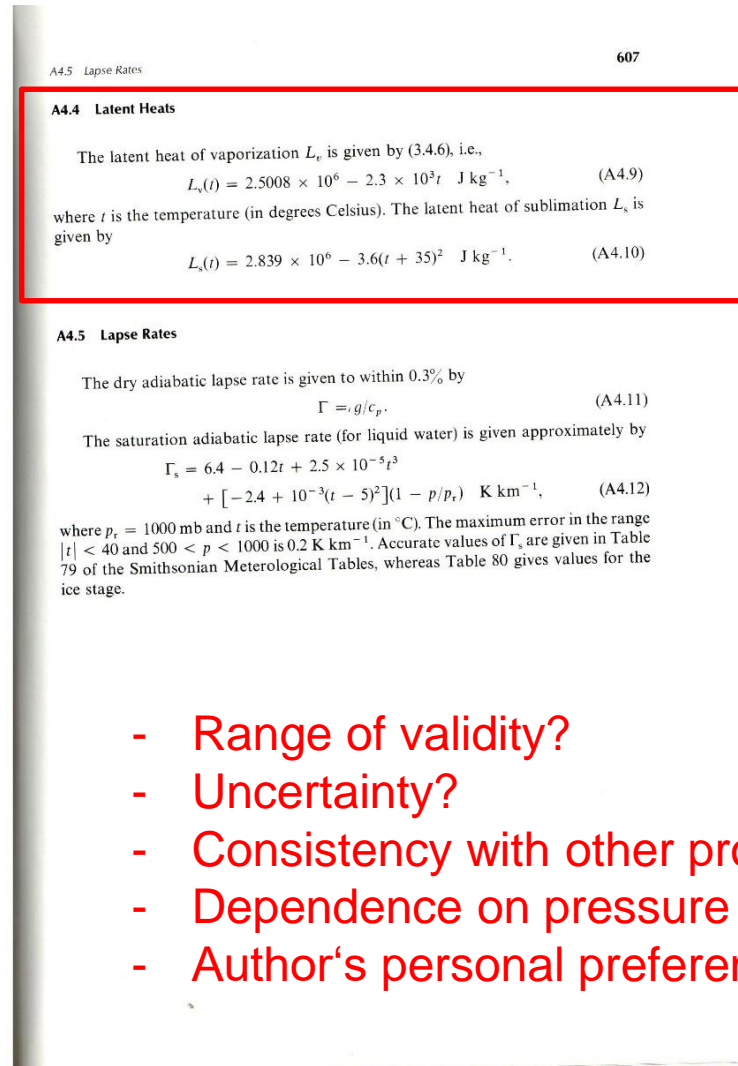
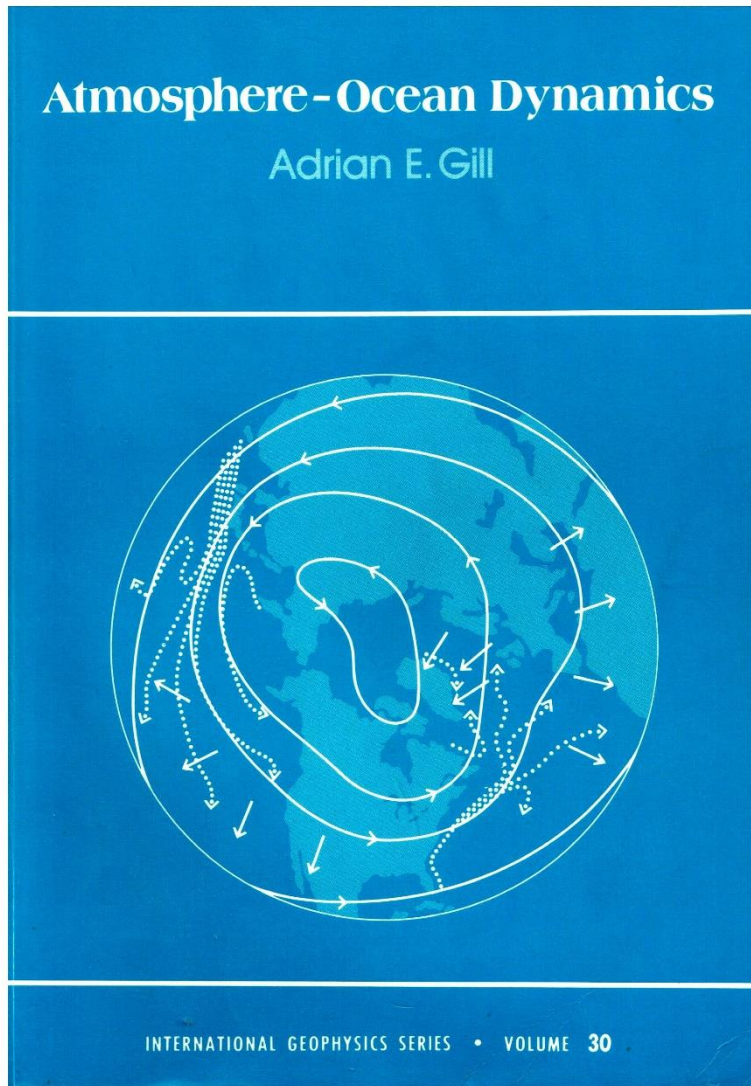
Conclusion from the examples:

Global climate change is extremely sensitive to thermodynamic processes at the ocean-atmosphere interface.

For proper balances of climatic energy and entropy fluxes in models and observation, a highly accurate, consistent and comprehensive thermodynamic standard framework is requisite in geophysics and climate research.

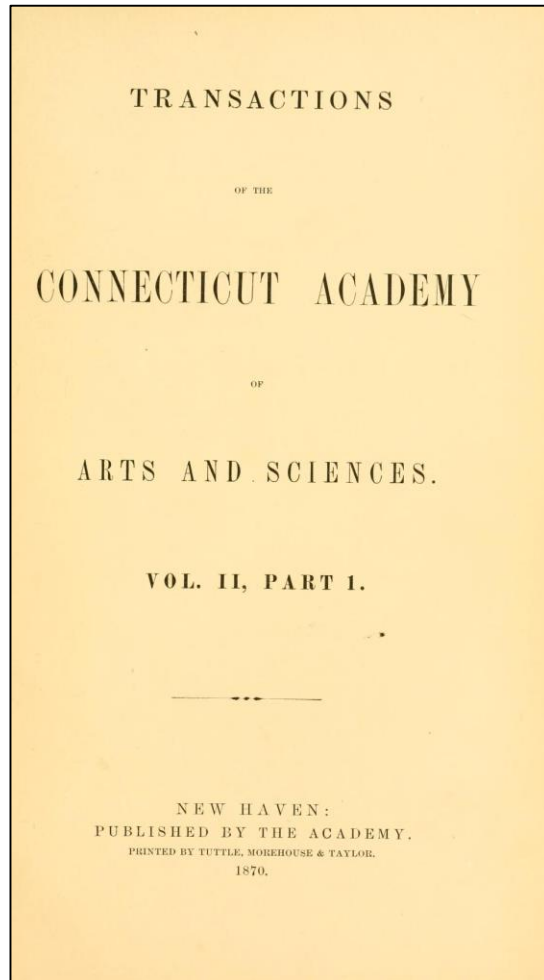
This appears to be obvious, but ...

... for the latent heat of evaporation,
a typical standard textbook situation is like this:



- Range of validity?
- Uncertainty?
- Consistency with other properties?
- Dependence on pressure or salinity?
- Author's personal preference?

Empirical Thermodynamic Potential: J. Willard Gibbs 1873



XIV. A METHOD OF GEOMETRICAL REPRESENTATION OF THE THERMODYNAMIC PROPERTIES OF SUBSTANCES BY MEANS OF SURFACES. BY J. WILLARD GIBBS.

THE leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, temperature, energy, and entropy of a given mass of the fluid in a state of thermodynamic equilibrium. The same is true of a solid in regard to those properties which it exhibits in processes in which the pressure is the same in every direction about any point of the solid.

But all the relations existing between these five quantities for any substance (three independent relations) may be deduced from the single relation existing for that substance between the volume, energy, and entropy. This may be done by means of the general equation,

$$d\varepsilon = t d\eta - p dv, \quad (1)^*$$

that is,
$$p = - \left(\frac{d\varepsilon}{dv} \right)_{\eta}, \quad (2)$$

$$t = \left(\frac{d\varepsilon}{d\eta} \right)_v, \quad (3)$$

where v , p , t , ε , and η denote severally the volume, pressure, absolute temperature, energy, and entropy of the body considered. The subscript letter after the differential coefficient indicates the quantity which is supposed constant in the differentiation.



Gibbs, J. W. (1873): A Method of Graphical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. Transactions of the Connecticut Academy of Arts and Science, 2, 382-404

Statistical Thermodynamic Potential: Ludwig Boltzmann 1877



Boltzmann Monument at the
Wiener Zentralfriedhof

Boltzmann's entropy formula:

$$S = k \ln W(E, V)$$

$W(E, V)$: Volume of the phase space
belonging to total energy E and volume V

Boltzmann entropy
 $S(E, V)$
is a thermodynamic potential



Boltzmann, L. (1877): Über die Beziehung zwischen dem zweiten Hauptsatz der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung resp. den Sätzen über das Wärmegleichgewicht. Sitzungsberichte der Akademie der Wissenschaften zu Wien 76, 373-435

Thermodynamic Potentials

Gibbs/Boltzmann: $E = E(S, V)$ or $e = \frac{E}{M} = e(\eta, \rho)$

1st Law: $de = Td\eta + \frac{p}{\rho^2}d\rho, \quad T = \frac{\partial e}{\partial \eta}, \quad p = \rho^2 \frac{\partial e}{\partial \rho}$

Helmholtz function: $f(T, \rho) = e - \eta \frac{\partial e}{\partial \eta}$ *Legendre Transform*

1st Law: $df = -\eta dT + \frac{p}{\rho^2}d\rho, \quad \eta = -\frac{\partial f}{\partial T}, \quad p = \rho^2 \frac{\partial f}{\partial \rho}$

Gibbs function: $g(T, p) = f + \rho \frac{\partial f}{\partial \rho}$ *Legendre Transform*

1st Law: $dg = -\eta dT + \rho^{-1}dp, \quad \eta = -\frac{\partial g}{\partial T}, \quad \rho^{-1} = \frac{\partial g}{\partial p}$

Enthalpy: $h(\eta, p) = g - T \frac{\partial g}{\partial T}$ *Legendre Transform*

1st Law: $dh = Td\eta + \rho^{-1}dp, \quad T = \frac{\partial h}{\partial \eta}, \quad \rho^{-1} = \frac{\partial h}{\partial p}$



humid air, 2-phase fluids

seawater, ice, 1-phase

adiabatic processes, mixing

Geophysics: potential temperature, potential density, potential enthalpy...

The international thermodynamic equation of seawater – 2010:

Calculation and use of thermodynamic properties

www.teos-10.org

Acknowledgements

This TEOS-10 Manual reviews and summarizes the work of the SCOR/IAPSO Working Group 127 on the Thermodynamics and Equation of State of Seawater. Dr John Gould and Professor Paola Malanotte-Rizzoli played pivotal roles in the establishment of the Working Group and we have enjoyed rock-solid scientific support from the officers of SCOR, IAPSO and IOC. TJMcD wishes to acknowledge fruitful discussions with Drs Jürgen Willebrand and Michael McIntyre regarding the contents of Appendix B. We have benefited from extensive comments on drafts of this manual by Dr Stephen Griffies and Dr Allyn Clarke. Louise Bell of CSIRO provided much appreciated advice on the layout of this document. TJMcD and DRJ wish to acknowledge partial financial support from the Wealth from Oceans National Flagship. This work contributes to the CSIRO Climate Change Research Program. This document is based on work partially supported by the U.S. National Science Foundation to SCOR under Grant No. OCE-0608600. FJM wishes to acknowledge the Oceanographic Section of the National Science Foundation and the National Oceanic and Atmospheric Administration for supporting his work.

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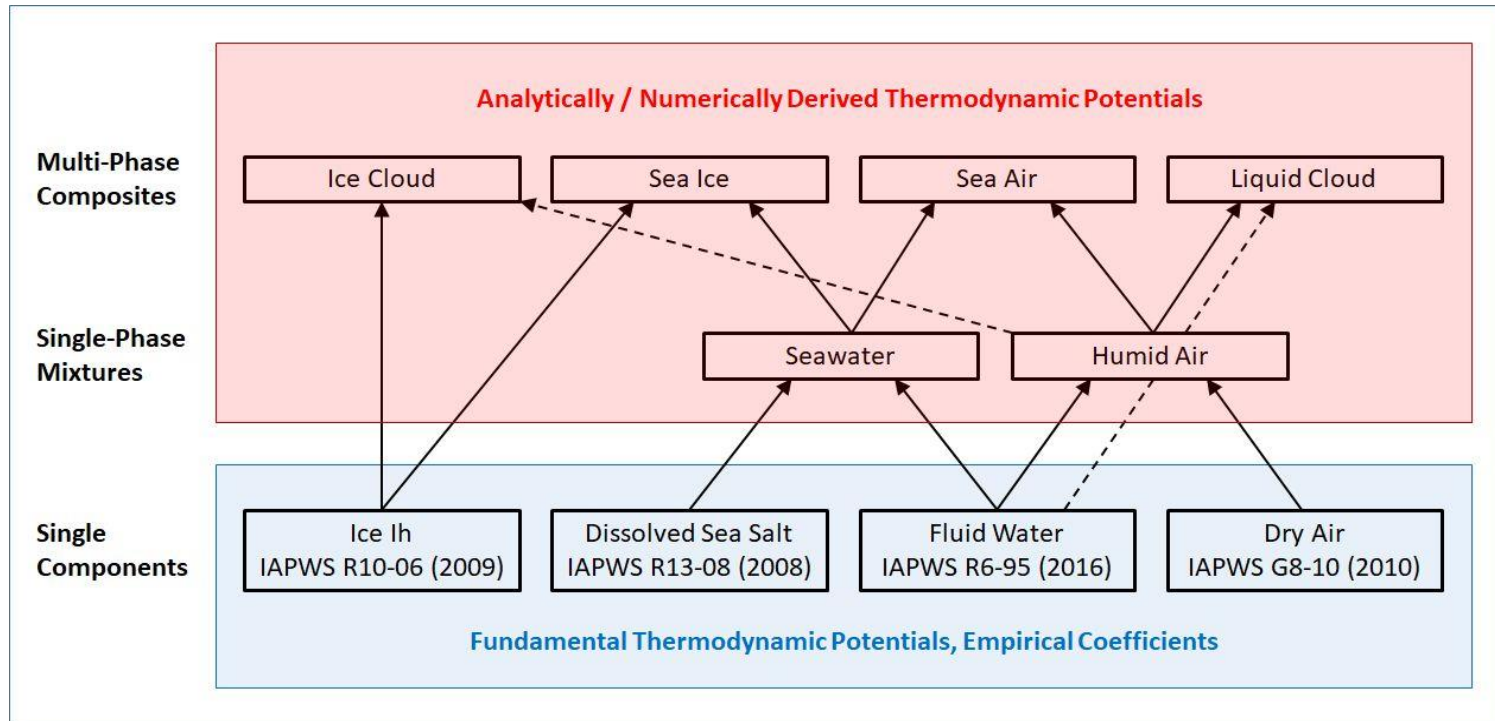


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Thermodynamic Potentials in TEOS-10



Empirical TD potentials compactly represent a wealth of experiments

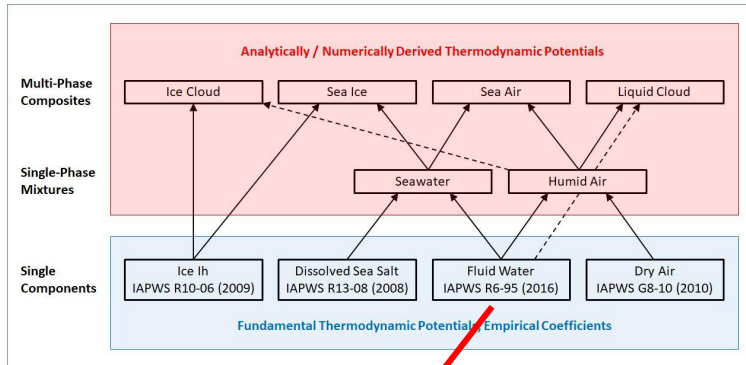
Axiomatic properties: consistency, completeness, independence



Feistel, R. et al. (2008): Mutually consistent thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography. Ocean Sci. 4, 275-291, www.ocean-sci.net/4/275/2008/

Feistel, R. (2012): TEOS-10: A New International Oceanographic Standard for Seawater, Ice, Fluid Water, and Humid Air, Int. J. Thermophys. 33, 1335–1351

Helmholtz Function of Fluid Water



$$\frac{f(\rho, T)}{RT} = \phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^r(\delta, \tau), \quad (4)$$

$$\phi^0 = \ln \delta + n_1^0 + n_2^0 \tau + n_3^0 \ln \tau + \sum_{i=4}^8 n_i^0 \ln \left[1 - e^{-\gamma_i^0 \tau} \right], \quad (5)$$

$$\phi^r = \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{e_i}} + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i (\delta - \varepsilon_i)^2 - \beta_i (\tau - \gamma_i)^2} + \sum_{i=55}^{56} n_i \Delta^b \delta \psi \quad (6)$$

www.iapws.org **IAPWS** IAPWS R6-95(2016)

The International Association for the Properties of Water and Steam

Dresden, Germany
September 2016

Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use

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This revised release replaces the corresponding revised releases of 2014 and 2009 (which replaced the original release of 1996), and contains 19 pages, including this cover page.

This Release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Dresden, Germany, 11-16 September, 2016. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, New Zealand, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, and associate members Argentina and Brazil, Australia, Egypt, France, Greece, and Switzerland. The President at the time of adoption of this document was Prof. Hans-Joachim Kretzschmar of Germany.

Summary

The formulation provided in this release is recommended for general and scientific use; further details about the formulation can be found in an article "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" by W. Wagner and A. Pruß [1]. This formulation provides the most accurate representation of the thermodynamic properties of the fluid phases of water substance over a wide range of conditions available at the time this release was prepared.

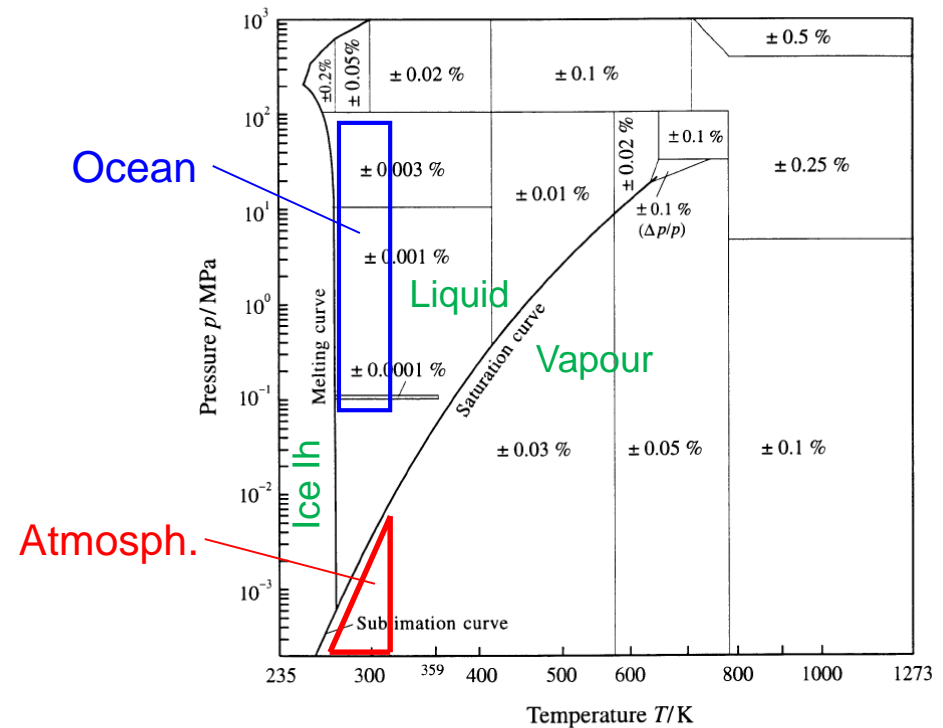
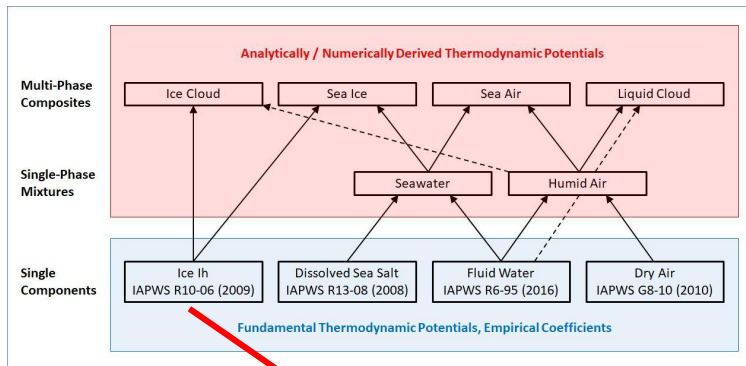


Fig. 1. Uncertainties in density, $\Delta\rho/\rho$, estimated for Eq. (4). In the enlarged critical region (triangle), the uncertainty is given as percentage uncertainty in pressure, $\Delta p/p$. This region is bordered by the two isochores 527 kg m^{-3} and 144 kg m^{-3} and by the 30 MPa isobar. The positions of the lines separating the uncertainty regions are approximate.

Gibbs Function of Ice Ih



$$g(T, p) = g_0(p) - s_0 T_t \tau + T_t \text{Re} \left(\sum_{k=1}^2 r_k \left[(t_k - \tau) \ln(t_k - \tau) + (t_k + \tau) \ln(t_k + \tau) - 2t_k \ln t_k - \frac{\tau^2}{t_k} \right] \right)$$

$$g_0(p) = \sum_{k=0}^4 g_{0k} (\pi - \pi_0)^k$$

$$r_2(p) = \sum_{k=0}^2 r_{2k} (\pi - \pi_0)^k,$$
(1)

www.iapws.org

IAPWS R10-06(2009)

The International Association for the Properties of Water and Steam

Doorwerth, The Netherlands
September 2009

Revised Release on the Equation of State 2006 for H₂O Ice Ih

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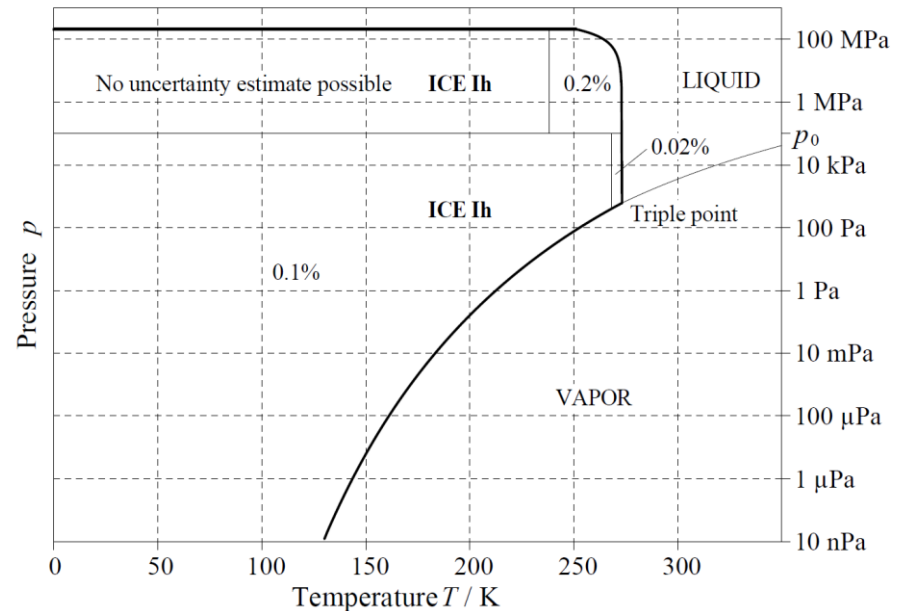


Fig. 1 Relative combined standard uncertainty of ice density, $u_c(\rho)/\rho$, Table 5, estimated for different regions of the T - p space. No experimental high-pressure data are available at low temperatures. This figure also illustrates the range of validity of the equation of state, Eq. (1).

Example for 2-Phase Equilibrium: Ice Ih + Liquid Water

Equal chemical potentials: $g^w(T, p) = g^{lh}(T, p)$

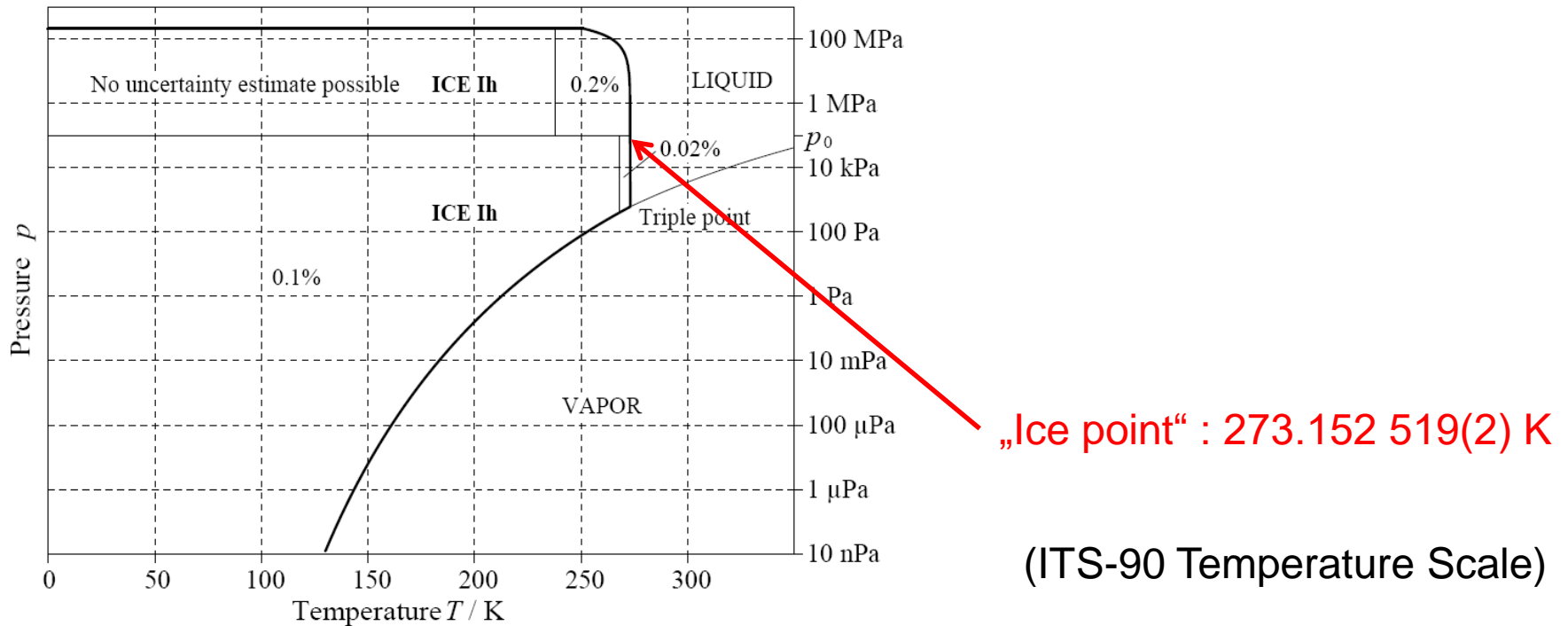


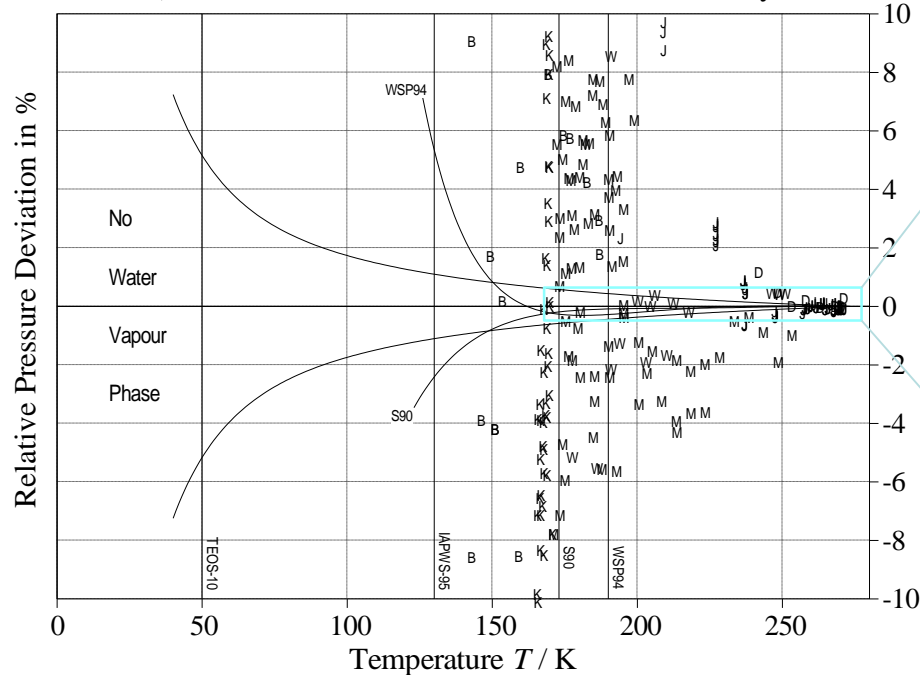
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Example for 2-Phase Equilibrium:

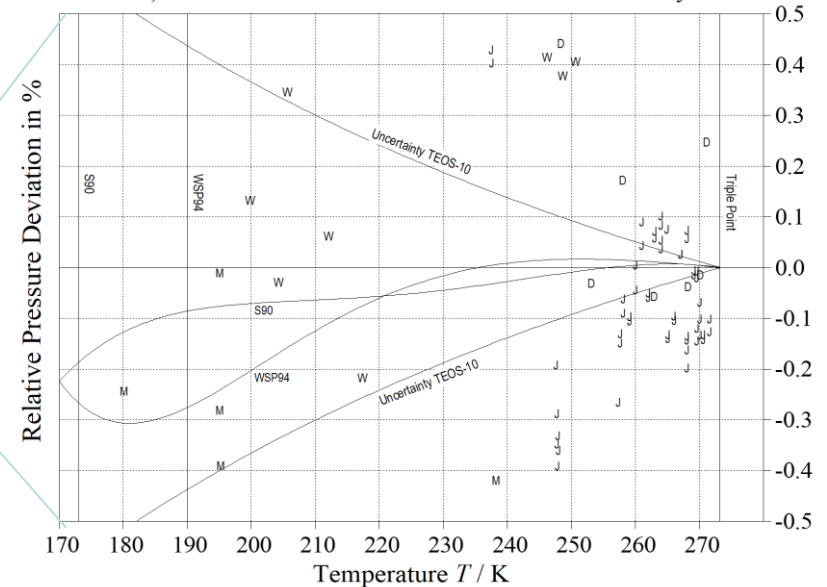
Ice Ih + Water Vapour

Equal chemical potentials: $g^v(T, p) = g^h(T, p)$

a) Sublimation Pressure Deviations and Uncertainty



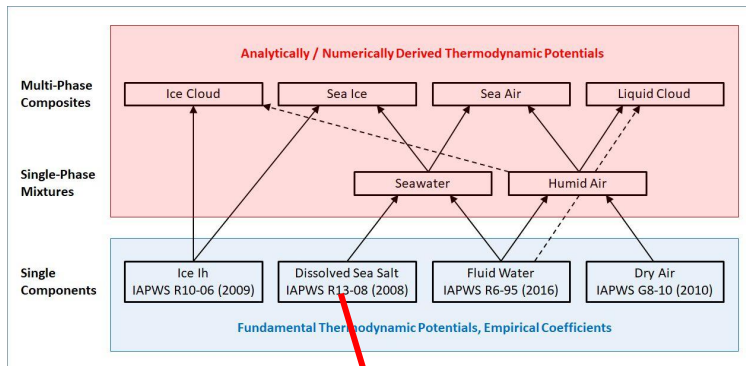
b) Sublimation Pressure Deviations and Uncertainty



TEOS-10 sublimation pressure

- is significantly more accurate than direct measurements
- is consistent with all thermodynamic properties of water and ice
- covers the range down to 50 K (at least)

Gibbs Function of Seawater



$$g(S, T, p) = g^w(T, p) + g^s(S, T, p). \quad (3)$$

The H_2O part is computed from the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, IAPWS-95 [3]. Reduced by $g^* = 1 \text{ J kg}^{-1}$, the saline part is the dimensionless polynomial-like function given by Eq. (4)

$$g^s(S, T, p) / g^* = \sum_{k=0}^5 \sum_{j=0}^6 \left(g_{1jk} \xi^2 \ln \xi + \sum_{i=2}^7 g_{ijk} \xi^i \right) \tau^j \pi^k, \quad (4)$$

with the reduced temperature $\tau = (T - T_0) / T^*$, the reduced pressure $\pi = (p - p_0) / p^*$, and the square root of the reduced salinity, $\xi = \sqrt{S / S^*}$. The reduced quantities τ , π and ξ vary from 0 to 1 in the oceanographic standard range. The constants T_0 , p_0 , T^* , p^* and S^* are given in Table 1.

www.iapws.org

IAPWS R13-08

The International Association for the Properties of Water and Steam

Berlin, Germany
September 2008

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

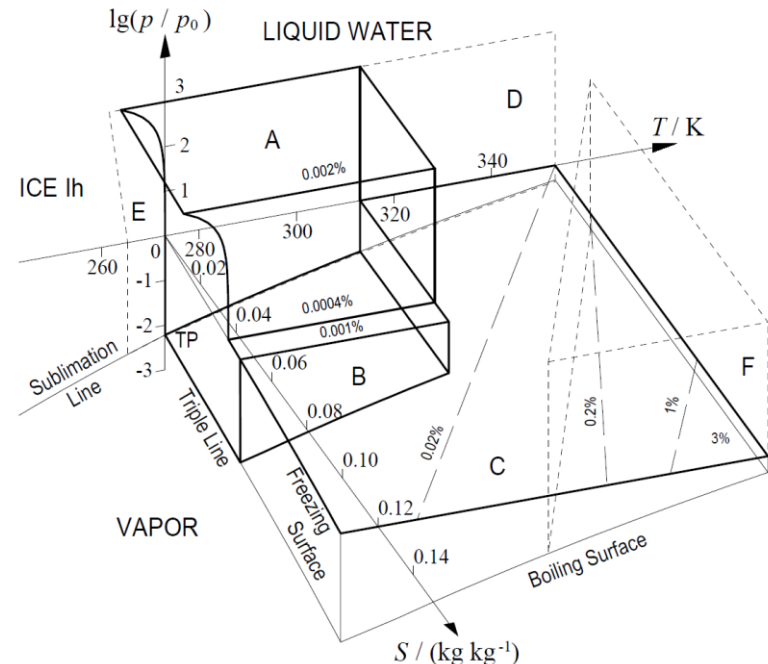
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Summary of Seawater Data Used for TEOS-10

Table 7

Summary of data used for the regression in this paper

Source	Quantity	S_A (g kg ⁻¹)	t (°C)	Points	r.m.s. required	r.m.s. result	Unit	Seawater
Millero et al. (1973a)	c_p^S	1–40	5–35	48	0.5	0.57	J kg ⁻¹ K ⁻¹	SS
Millero and Pierrot (2005)	c_p	1–35	10–40	41	1.0	1.3	J kg ⁻¹ K ⁻¹	ns
Bromley et al. (1967)	c_p	11–117	2–80	221	4	3.5	J kg ⁻¹ K ⁻¹	JS
Robinson (1954)	p^{vap}	18–40	25	13	0.02	0.002	%	SS
Bromley et al. (1974)	t_{boil}	6–70	60–80	32	1	1.3	mK	DS
Doherty and Kester (1974)	t_f	4–40	–2 to 0	32	3	2.0	J kg ⁻¹	AS
Feistel and Marion (2007)	t_f	5–110	–7 to 0	22	10	1.5	J kg ⁻¹	MS
Bromley (1968)	Δh	0–108	25	33	1	0.75	J kg ⁻¹	JS
Millero et al. (1973b)	Δh	1–42	0–30	120	10	3.3	J kg ⁻¹	SS
Connors (1970)	Δh	10–61	2–25	19	10	7.2	J kg ⁻¹	ns
Limiting law (6.7)	g^{LL}	35	–5 to 95	21	1	0.09	J kg ⁻¹	RS
Total		0–117	–7 to 95	602				

All data are at atmospheric pressure. Seawater: AS: Sargasso Sea (Atlantic), DS: San Diego (Pacific), JS: La Jolla (Pacific), MS: model seawater, RS: reference seawater, SS: standard (Atlantic) seawater, ns: not specified.

Table 8

Summary of PVT data which were used for the determination of the former 2003 Gibbs function polynomial coefficients by regression

Source	Quantity	S_A (g kg ⁻¹)	t (°C)	p (Mpa)	u_c	r.m.s.	Unit	Seawater
Millero et al. (1976)	ρ	0.5–40	0–40	0	4	4.1	ppm	SS
Poisson et al. (1980)	ρ	5–42	0–30	0	4	4.0	ppm	SS
Poisson and Gadhoumi (1993)	ρ	34–50	15–30	0	10	11.3	ppm	SS
Chen and Millero (1976)	ρ	5–40	0–40	0–100	10	11.0	ppm	SS
Bradshaw and Schleicher (1970)	ρ^S	30–40	–2 to 30	1–100	4	2.6	ppm	SS
Caldwell (1978)	α	10–30	–6 to 1	0.7–33	0.6	0.73	ppm K ⁻¹	OS
Del Grosso (1974)	c	29–43	0–35	0–2	5	1.7	cm s ⁻¹	SS
Del Grosso (1974)	c	29–43	0–30	0.1–5	5	1.2	cm s ⁻¹	SS
Del Grosso (1974)	c	33–37	0–5	0–100	5	3.5	cm s ⁻¹	SS
Total		0.5–43	–6 to 40	0–100				

u_c is the estimated standard uncertainty of the particular data set, r.m.s. was the accuracy of the fit. Seawater: OS: Oregon (Pacific), SS: Standard (Atlantic).

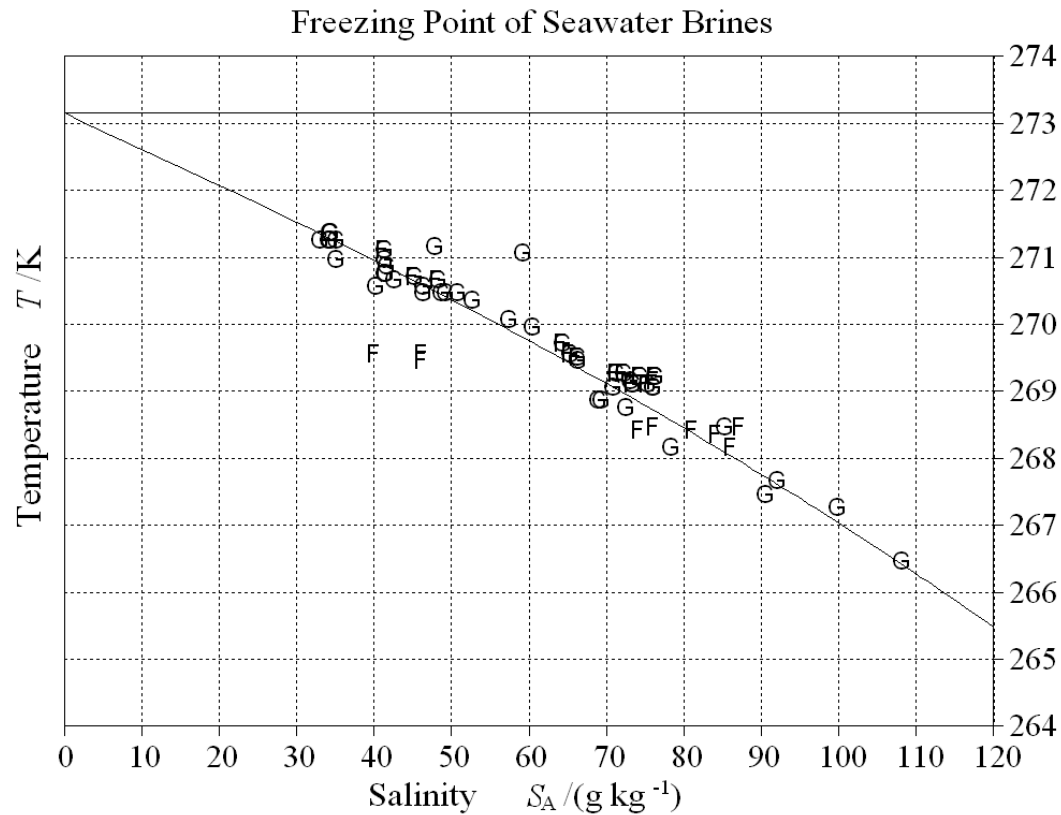


Feistel, R. (2008): A Gibbs Function for Seawater Thermodynamics for -6 °C to 80 °C and Salinity up to 120 g/kg. Deep-Sea Research I, 55, 1639-1671

Seawater + Ice: Antarctic Sea Ice Data

Equilibrium ice – seawater:

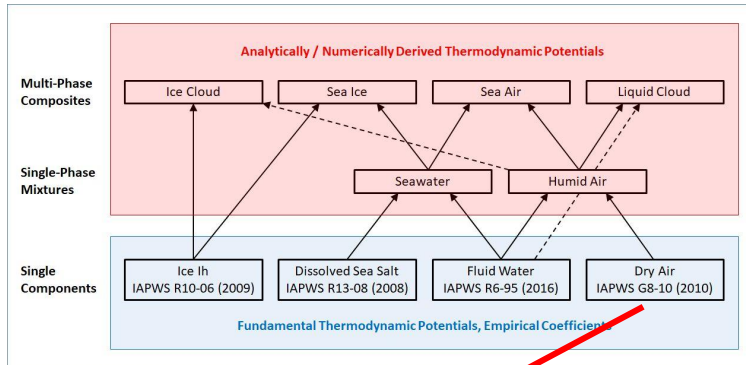
$$g^{\text{Ih}} = g^{\text{SW}} - S_A \frac{\partial g^{\text{SW}}}{\partial S_A}$$



F: Michael Fischer, Diploma Thesis, University of Leipzig 2009

G: Markus Gleitz et al., Marine Chemistry 51 (1995) 81-91

Helmholtz Function of Humid Air



$$f^{\text{AV}}(A, T, \rho) = (1 - A)f^{\text{V}}(T, \rho^{\text{V}}) + Af^{\text{A}}(T, \rho^{\text{A}}) + f^{\text{mix}}(A, T, \rho). \quad (1)$$

$$f^{\text{V}}(T, \rho^{\text{V}}) \equiv f^{\text{IAPWS-95}}(T, \rho^{\text{V}}), \quad (2)$$

$$f^{\text{A}}(T, \rho^{\text{A}}) = \frac{R^{\text{L}}T}{M_{\text{A}}} [\alpha^{\text{id}}(\tau, \delta) + \alpha^{\text{res}}(\tau, \delta)]. \quad (3)$$

$$\alpha^{\text{id}}(\tau, \delta) = \ln \delta + \sum_{i=1}^5 n_i^0 \tau^{i-4} + n_6^0 \tau^{1.5} + n_7^0 \ln \tau + n_8^0 \ln[1 - \exp(-n_{11}^0 \tau)] \\ + n_9^0 \ln[1 - \exp(-n_{12}^0 \tau)] + n_{10}^0 \ln[2/3 + \exp(n_{13}^0 \tau)] \quad (4)$$

$$\alpha^{\text{res}}(\tau, \delta) = \sum_{k=1}^{10} n_k \delta^{i_k} \tau^{j_k} + \sum_{k=11}^{19} n_k \delta^{i_k} \tau^{j_k} \exp(-\delta^{l_k}). \quad (5)$$

$$f^{\text{mix}}(A, T, \rho) = \frac{2A(1-A)\rho RT}{M_{\text{A}}M_{\text{W}}} \left\{ B^{\text{AW}}(T) + \frac{3}{4} \rho \left[\frac{A}{M_{\text{A}}} C^{\text{AAW}}(T) + \frac{(1-A)}{M_{\text{W}}} C^{\text{AWW}}(T) \right] \right\}. \quad (8)$$

www.iapws.org

IAPWS G8-10

The International Association for the Properties of Water and Steam

Niagara Falls, Canada
July 2010

**Guideline on an Equation of State for Humid Air in Contact with Seawater and Ice,
Consistent with the IAPWS Formulation 2008 for the
Thermodynamic Properties of Seawater**

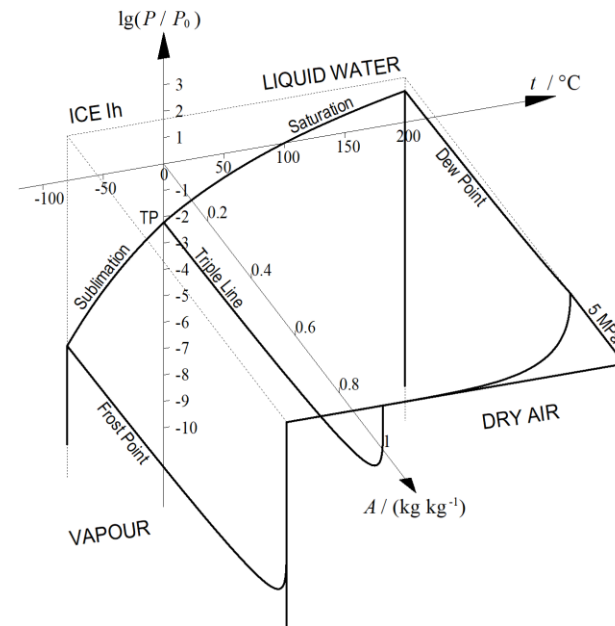
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This Guideline contains 21 pages, including this cover page.

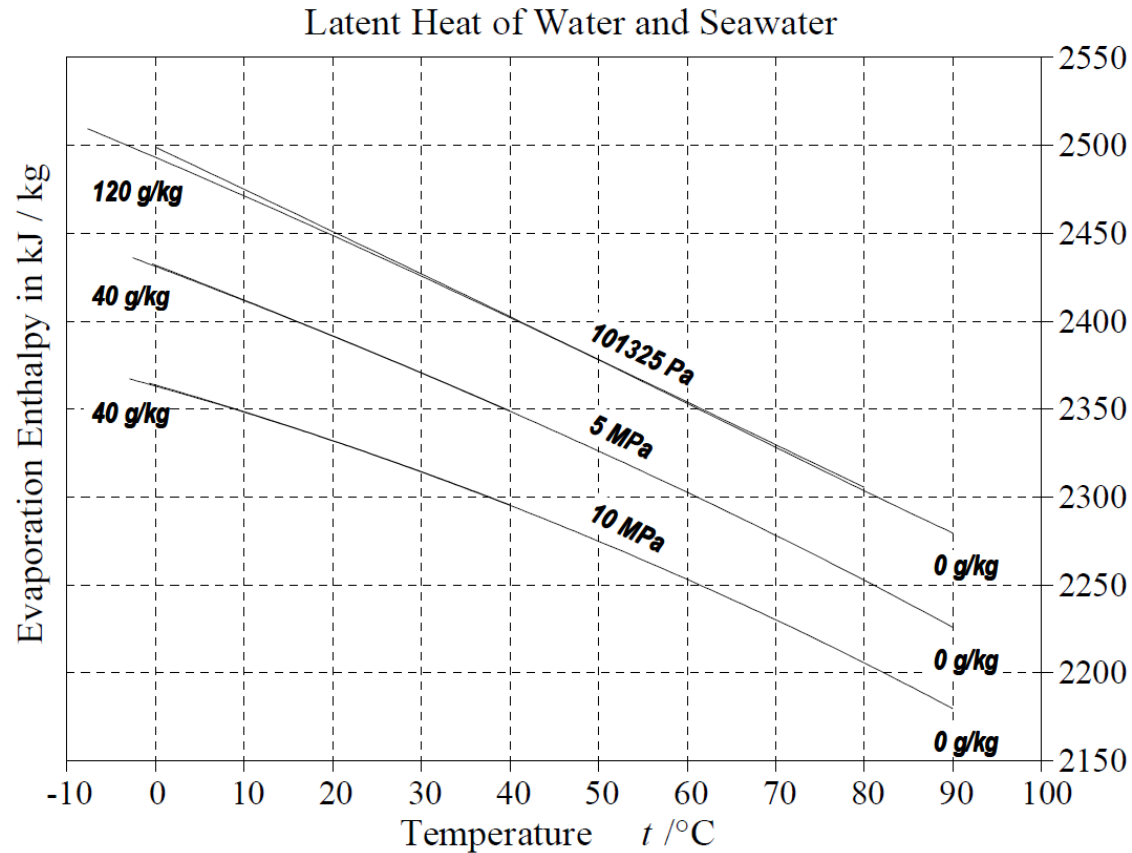
This Guideline has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Niagara Falls, Canada, 18-23 July, 2010, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Japan, Russia, the United States of America, and associate members Argentina and Brazil, Italy, and Switzerland.



Seawater + Humid Air:

Latent Heat of Evaporation

$$L = h^{AV} - A \frac{\partial h^{AV}}{\partial A} - h^{SW} + S_A \frac{\partial h^{SW}}{\partial S_A}$$



Feistel, R. et al. (2010): Thermodynamic properties of sea air. Ocean Sci. 6, 91–141, www.ocean-sci.net/6/91/2010/

Calculating TEOS-10 Properties

Computation of Seawater Properties from the Gibbs Function

Table S7a: Thermodynamic properties derived from the Gibbs function (4.4) of seawater, $g^{\text{sw}}(S_A, T, P)$, section 4.2, and its temperature, pressure and salinity derivatives. The superscript SW on g is suppressed for simplicity.

Quantity Library function	Formula	SI Unit	Eq.
Density sea_density_si	$\rho = g_P^{-1}$	$\frac{\text{kg}}{\text{m}^3}$	(S7.1)
Specific entropy sea_entropy_si	$\eta = -g_T$	$\frac{\text{J}}{\text{kgK}}$	(S7.2)
Specific enthalpy sea_enthalpy_si	$h = g - T g_T$	$\frac{\text{J}}{\text{kg}}$	(S7.3)
Specific internal energy sea_internal_energy_si	$u = g - T g_T - P g_P$	$\frac{\text{J}}{\text{kg}}$	(S7.4)
Specific Helmholtz energy	$f = g - P g_P$	$\frac{\text{J}}{\text{kg}}$	(S7.5)
Specific isobaric heat capacity sea_cp_si	$c_P = -T g_{TT}$	$\frac{\text{J}}{\text{kgK}}$	(S7.6)
Specific isochoric heat capacity	$c_v = T(g_{TP}^2 - g_{TT} g_{PP}) / g_{PP}$	$\frac{\text{J}}{\text{kgK}}$	(S7.7)
Isothermal compressibility sea_kappa_t_si	$\kappa_T = -g_{PP} / g_P$	$\frac{1}{\text{Pa}}$	(S7.8)
Isentropic compressibility sea_kappa_s_si	$\kappa_s = (g_{TP}^2 - g_{TT} g_{PP}) / (g_P g_{TT})$	$\frac{1}{\text{Pa}}$	(S7.9)
Sound speed sea_soundspeed_si	$c = g_P \sqrt{g_{TT} / (g_{TP}^2 - g_{TT} g_{PP})}$	$\frac{\text{m}}{\text{s}}$	(S7.10)
Adiabatic lapse rate sea_lapserate_si	$\Gamma = -g_{TP} / g_{TT}$	$\frac{\text{K}}{\text{Pa}}$	(S7.11)
Chemical potential of water sea_chempot_h2o_si	$\mu^{\text{w}} = g - S_A g_S$	$\frac{\text{J}}{\text{kg}}$	(S7.12)
Chemical potential of sea salt	$\mu^{\text{s}} = g + (1 - S_A) g_S$	$\frac{\text{J}}{\text{kg}}$	(S7.13)
Barodiffusion ratio	$k_P = P g_{SP} / g_{SS}$	1	(S7.14)



Feistel, R. et al. (2010): Numerical implementation and oceanographic application of the thermodynamic potentials of liquid water, water vapour, ice, seawater and humid air – Part 1: Background and equations. Ocean Science 6, 633–677, www.ocean-sci.net/6/633/2010/

TEOS-10 Open Source Code Libraries


Seawater-Ice-Air Library SIA (VB6, Fortran)

- Directly exploits implemented IAPWS formulations
- Implements about 500 functions (plus 191 auxiliary)

Gibbs-Seawater Library GSW (Matlab, Fortran, C, PHP)

- Faster correlation equations of SIA data for oceanography
- Oceanographic properties not implemented in SIA
- Implements about 200 functions

Feistel, R. et al. (2010): Numerical implementation and oceanographic application of the thermodynamic potentials of liquid water, water vapour, ice, seawater and humid air – Part 1: Background and equations. Ocean Science 6, 633–677, www.ocean-sci.net/6/633/2010/

 Wright, D.G. et al. (2010): Numerical implementation and oceanographic application of the thermodynamic potentials of liquid water, water vapour, ice, seawater and humid air – Part 2: The library routines. Ocean Science 6, 695-718, www.ocean-sci.net/6/695/2010/

McDougall, Barker, P.M. (2011): Getting started with TEOS-10 and the Gibbs Seawater (GSW) Oceanographic Toolbox, 28pp., SCOR/IAPSO WG127, ISBN 978-0-646-55621-5, www.teos-10.org

Roquet, F. et al. (2015): Accurate polynomial expressions for the density and specific volume of seawater using the TEOS-10 standard. Ocean Modelling 90, 29–43

TEOS-10

SIA Library modules

SIA Library functions

(Fortran & VB source codes)

(S15) Sea_3b

Uses

constants_0, sal_2, flu_3a,
sea_3a (convert_0, maths_0,
flu_1, sal_1)

Public Routines

sea_h_si

sea_h_contraction_h_si

(S16) Air_3b

Uses

constants_0, convert_0,
air_1, air_2, air_3a
(maths_0, flu_1)

Public Routines

air_g_chempot_vap_si
air_g_compressibility
factor_si

air_g_contraction_si

air_g_cp_si

air_g_cv_si

air_g_density_si

air_g_enthalpy_si

air_g_entropy_si

air_g_expansion_si

air_g_gibbs_energy_si

air_g_internal_energy_si

air_g_kappa_s_si

air_g_kappa_t_si

air_g_lapserate_si

air_g_soundspeed_si

chk_lemmon_etal_2000

Table S16 (Air_3b): Thermodynamic properties of humid air in terms of the mass fraction of dry air in humid air in kg kg^{-1} , the absolute temperature in K and the pressure in Pa. The quantities here are all conveniently expressed in terms of the Gibbs potential function (S16.9). (See Part I, section 4.4.)

(S16) Air_3b Module

Function call	Mathematical equation	Unit	Comments
air_g_chempot_vap_si: chemical potential of vapour in humid air (S16.1)			
air_g_chempot_vap_si(a, t, p) a = A / (kg kg^{-1}) t = T / K p = P / Pa	$g^{\text{AV}} - A \frac{\partial g^{\text{AV}}}{\partial A}$	$\frac{\text{J}}{\text{kg}}$	g^{AV} is the Gibbs function for moist air (S13.2) and subscripts indicate partial differentiation.
air_g_compressibilityfactor_si: compressibility factor for moist air (S16.2)			
air_g_compressibilityfactor_si(a, t, p) a = A / (kg kg^{-1}) t = T / K p = P / Pa	$\frac{P}{\rho R_{\text{AV}} T}$ $R_{\text{AV}} = R \left[\frac{1-A}{M^{\text{W}}} + \frac{A}{M^{\text{A}}} \right]$	1	R_{AV} is the specific molar gas constant for moist air.
air_g_contraction_si: contraction coefficient of humid air (S16.3)			
air_g_contraction_si(a, t, p) a = A / (kg kg^{-1}) t = T / K p = P / Pa	$\beta = - \frac{g_{\text{AP}}^{\text{AV}}}{g_{\text{P}}^{\text{AV}}}$	$\frac{\text{kg}}{\text{kg}}$	see comments for (S16.1)

(S18) Air_3c

Uses

constants_0, convert_0,

Gibbs SeaWater (GSW) Oceanographic Toolbox of TEOS-10



water column properties, based on the 48-term expression for density, $\hat{\rho}(S_A, \Theta, p)$

gsw_Nsquared	buoyancy (Brunt-Väisälä) frequency squared (N^2)
gsw_Turner_Rsubrho	Turner angle & Rsubrho
gsw_IPV_vs_fInsquared_ratio	ratio of the vertical gradient of potential density (with reference pressure, p_{ref}), to the vertical gradient of locally-referenced potential density

neutral properties, based on the 48-term expression for density, $\hat{\rho}(S_A, \Theta, p)$

gsw_isopycnal_slope_ratio	ratio of the slopes of isopycnals on the SA-CT diagram for p & p_{ref}
gsw_isopycnal_vs_ntp_CT_ratio	ratio of the gradient of CT in a potential density surface to that in the neutral tangent plane
gsw_ntp_pt_vs_CT_ratio	ratio of gradients of pt & CT in a neutral tangent plane

geostrophic streamfunctions, based on the 48-term expression for density, $\hat{\rho}(S_A, \Theta, p)$

gsw_geo_strf_dyn_height	dynamic height anomaly
gsw_geo_strf_dyn_height_po	dynamic height anomaly for piecewise constant profiles
gsw_geo_strf_isopycnal	approximate isopycnal geostrophic streamfunction
gsw_geo_strf_isopycnal_po	approximate isopycnal geostrophic streamfunction for piecewise constant profiles
gsw_geo_strf_Cunningham	Cunningham geostrophic streamfunction
gsw_geo_strf_Montgomery	Montgomery geostrophic streamfunction
gsw_geo_strf_steric_height	dynamic height anomaly divided by 9.7983 m s^{-2}

geostrophic velocity

gsw_geostrophic_velocity	geostrophic velocity
--------------------------	----------------------

derivatives of entropy, CT and pt

gsw_CT_first_derivatives	first derivatives of Conservative Temperature
gsw_CT_second_derivatives	second derivatives of Conservative Temperature
gsw_entropy_first_derivatives	first derivatives of entropy
gsw_entropy_second_derivatives	second derivatives of entropy
gsw_pt_first_derivatives	first derivatives of potential temperature
gsw_pt_second_derivatives	second derivatives of potential temperature

seawater properties at freezing temperatures

gsw_CT_freezing	Conservative Temperature freezing temperature of seawater
gsw_CT_freezing_poly	Conservative Temperature freezing temperature of seawater (polynomial)
gsw_t_freezing	in-situ freezing temperature of seawater
gsw_t_freezing_poly	in-situ freezing temperature of seawater (polynomial)
gsw_brineSA_CT	Absolute Salinity of seawater at the freezing temperature (for given CT)
gsw_brineSA_CT_poly	Absolute Salinity of seawater at the freezing temperature (for given CT) (polynomial)
gsw_brineSA_t	Absolute Salinity of seawater at the freezing temperature (for given t)
gsw_brineSA_t_poly	Absolute Salinity of seawater at the freezing temperature (for given t) (polynomial)
gsw_pressure_freezing_CT	pressure of seawater at the freezing temperature (for given CT)
gsw_CT_freezing_first_derivatives	first derivatives of Conservative Temperature freezing temperature of seawater
gsw_t_freezing_first_derivatives	first derivatives of in-situ freezing temperature of seawater
gsw_latentheat_melting	latent heat of melting of ice into seawater (isobaric melting enthalpy)

thermodynamic interaction between ice Ih and seawater

gsw_melting_ice_SA_CT_ratio	SA to CT ratio when ice melts in seawater
gsw_melting_ice_equilibrium_SA_CT_ratio	SA to CT ratio when ice melts into seawater, near equilibrium
gsw_melting_ice_into_seawater	SA and CT when ice melts in seawater
gsw_ice_fraction_to_freeze_seawater	ice mass fraction to freeze seawater
gsw_frazil_ratios	ratios of SA, CT and P changes during frazil ice formation

thermodynamic interaction between sea ice and seawater

gsw_melting_seaice_SA_CT_ratio	SA to CT ratio when sea ice melts in seawater
gsw_melting_seaice_equilibrium_SA_CT_ratio	SA to CT ratio when sea ice melts into seawater, near equilibrium
gsw_melting_seaice_into_seawater	SA and CT when sea ice melts in seawater
gsw_seaice_fraction_to_freeze_seawater	sea ice mass fraction to freeze seawater

thermodynamic properties of ice Ih

gsw_rho_ice	in-situ density of ice
gsw_alpha_wrt_t_ice	thermal expansion coefficient of ice with respect to in-situ temperature
gsw_specvol_ice	specific volume of ice
gsw_pressure_coefficient_ice	pressure coefficient of ice
gsw_sound_speed_ice	sound speed of ice (compression waves)
gsw_kappa_ice	isentropic compressibility of ice
gsw_kappa_const_t_ice	isothermal compressibility of ice
gsw_internal_energy_ice	internal energy of ice
gsw_enthalpy_ice	enthalpy of ice
gsw_entropy_ice	entropy of ice
gsw_cp_ice	isobaric heat capacity of ice
gsw_chem_potential_water_ice	chemical potential of water in ice
gsw_Helmholtz_energy_ice	Helmholtz energy of ice
gsw_adiabatic_lapse_rate_ice	adiabatic lapse rate of ice
gsw_pt0_from_t_ice	potential temperature of ice with reference pressure of 0 dbar
gsw_pt_from_t_ice	potential temperature of ice
gsw_t_from_pt0_ice	in-situ temperature from potential temperature of ice with p_{ref} of 0 dbar
gsw_pot_enthalpy_from_pt_ice	potential enthalpy from potential temperature of ice
gsw_pt_from_pot_enthalpy_ice	potential temperature from potential enthalpy of ice
gsw_pot_enthalpy_from_pt_ice_poly	potential enthalpy from potential temperature of ice (polynomial)
gsw_pt_from_pot_enthalpy_ice_poly	potential temperature from potential enthalpy of ice (polynomial)

http://www.teos-10.org/pubs/gsw/html/gsw_contents.html

Beyond TEOS-10

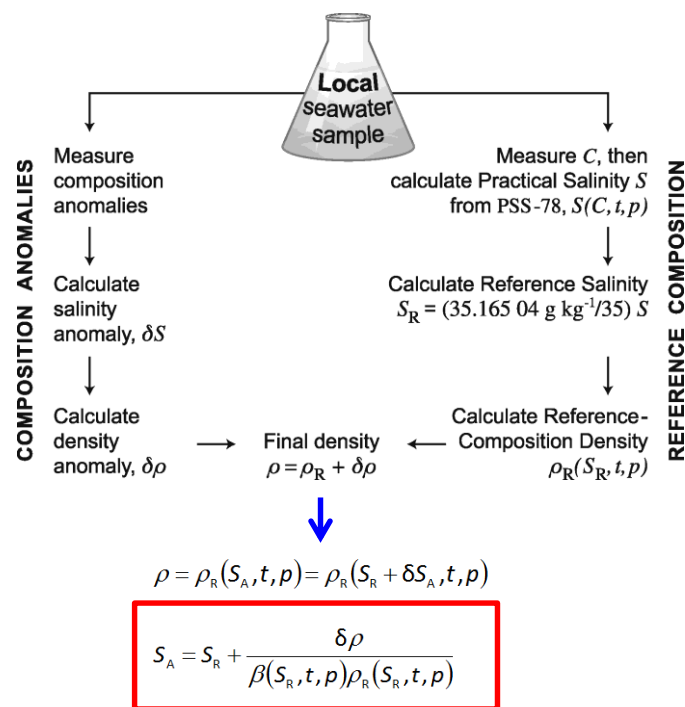
The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale

Frank J. Millero^{a,*}, Rainer Feistel^b, Daniel G. Wright^c, Trevor J. McDougall^d

IAPSO Standard Seawater: Salinity S_R in g/kg

Solute, i	$10^7 X_i$ (Definition)	$X_i A_i$	W_i	w_i g kg ⁻¹	r_i	r_i / A_i mol g ⁻¹	x_i mol kg ⁻¹	m_i mol kg ⁻¹
Properties of sea salt of Reference Composition				Properties of KCl-normalized Reference Seawater				
Na ⁺	4188071	9.6282786	0.3065958	10.78145	0.556492	0.02420609	0.4689674	0.4860597
Mg ²⁺	471678	1.1464134	0.0365055	1.28372	0.066260	0.00272619	0.0528171	0.0547421
Ca ²⁺	91823	0.3680082	0.0117186	0.41208	0.021270	0.00053072	0.0102821	0.0106568
K ⁺	91159	0.3564162	0.0113495	0.39910	0.020600	0.00052688	0.0102077	0.0105797
Sr ²⁺	810	0.0070972	0.0002260	0.00795	0.000410	0.00000468	0.0000907	0.0000940
Cl ⁻	4874839	17.2827667	0.5503396	19.35271	0.998904	0.02817545	0.5458696	0.5657647
SO ₄ ²⁻	252152	2.4222377	0.0771319	2.71235	0.140000	0.00145738	0.0282352	0.0292643
HCO ₃ ⁻	15340	0.0935998	0.0029805	0.10481	0.005410	0.00008866	0.0017177	0.0017803
Br ⁻	7520	0.0600878	0.0019134	0.06728	0.003473	0.00004346	0.0008421	0.0008728
CO ₃ ²⁻	2134	0.0128059	0.0004078	0.01434	0.000740	0.00001233	0.0002390	0.0002477
B(OH) ₄ ⁻	900	0.0070956	0.0002259	0.00795	0.000410	0.00000520	0.0001008	0.0001045
F ⁻	610	0.0011589	0.0000369	0.00130	0.000067	0.00000353	0.0000683	0.0000708
OH ⁻	71	0.0001208	0.0000038	0.00014	0.000007	0.00000041	0.0000080	0.0000082
B(OH) ₃	2807	0.0173565	0.0005527	0.01944	0.001003	0.00001622	0.0003143	0.0003258
CO ₂	86	0.0003785	0.0000121	0.00042	0.000022	0.00000050	0.0000096	0.0000100
Sum	10000000	31.4038218	1.0000000	35.16504	1.815069	0.05779770	1.1197690	1.1605813
H ₂ O				964.83496	49.800646	2.76435771	53.5565138	55.5084714
Sum				1000.00000	51.615714		54.6762834	56.6690528

Composition Anomalies



Global Salinity Anomalies (ignored before TEOS-10)

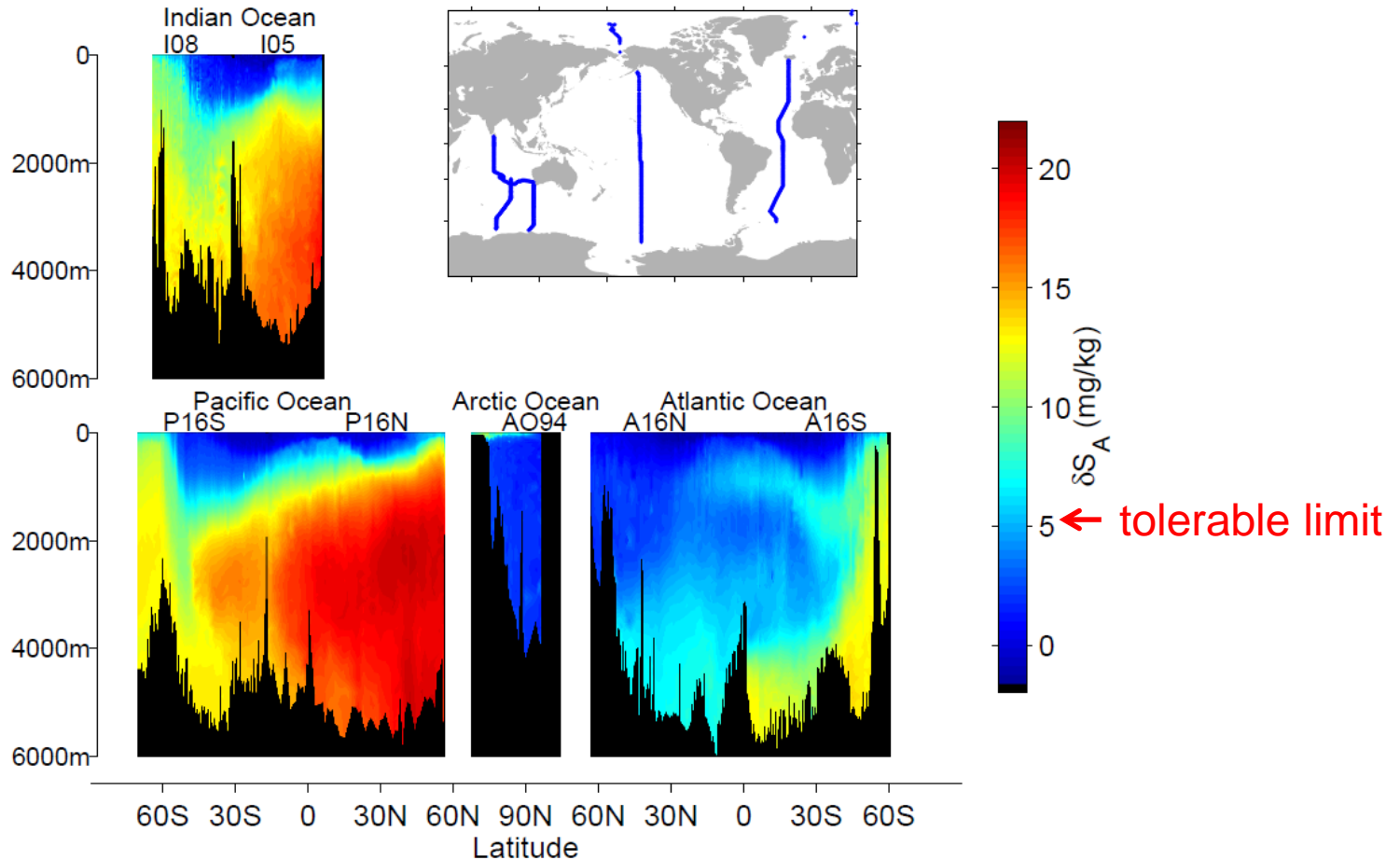


Fig. 1. Salinity anomalies δS_A for trans-oceanic hydrographic sections in different oceanic basins. Values are calculated by the numerical model of Pawlowicz et al., (2011) using archived observations of carbon parameters and nutrients along these sections. Data obtained from the CLIVAR and Carbon Hydrographic Data Office (cchdo.ucsd.edu).

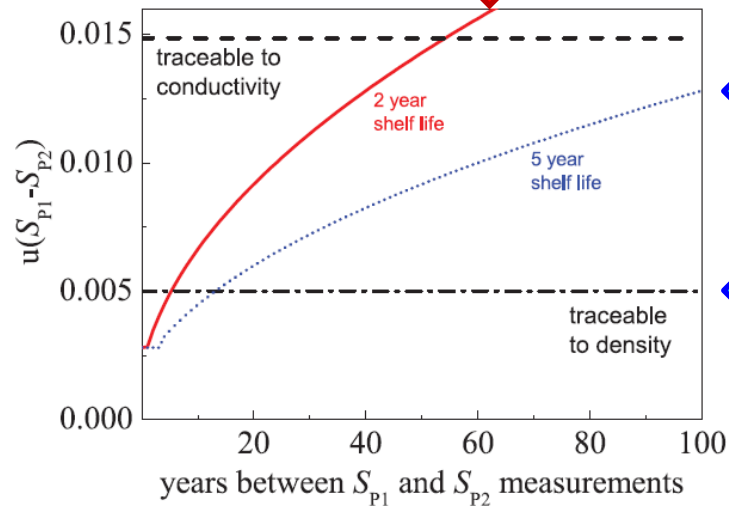


Pawlowicz, R., McDougall, T., Feistel, R., Tailleux, R. (2012): An historical perspective on the development of the Thermodynamic Equation of Seawater – 2010. Ocean Science 8, 161–174, www.ocean-sci.net/8/161/2012/

Metrological Traceability of Seawater Salinity

- Salinity measurements are currently not traceable to the SI

Metrologia 53 (2016) R12



Uncertainty growth risk

Required stable uncertainty level

Figure 1. Uncertainty of the difference of two independent salinity measurements, S_{p1} and S_{p2} , versus the time elapsed between the measurements. The uncertainty increases for results traceable to the conductance ratio of SSW, depending on the assumed shelf life of SSW: the solid red line to 2 years (Culkin and Ridout 1998), the dotted blue line to 5 years (Bacon *et al* 2007). In contrast, the uncertainties do not increase with time if the results are traceable to the SI. The dash-dotted line refers to results traceable to density which would provide a better bound on uncertainty after about a decade, the dashed line to SI conductivity standards, which would not provide a useful bound until measurements were separated by many decades.

Aim:
Density definition of salinity
+
Keep established practice



IAPWS-BIPM meeting, 7 February 2012, Pavillon de Breteuil International Bureau of Weights and Measures, Paris-Sèvres



IAPWS



Participants of the IAPWS-BIPM Meeting on 7 February 2012 at the BIPM headquarter, Pavillon de Breteuil at Sèvres near Paris, from left to right: Dan Friend, Karol Daucik, Jeff Cooper, Alain Picard, Petra Spitzer, Rainer Feistel, Michael Kuehne, Andy Henson, Robert Wielgosz.

16th International Conference on the Properties of Water and Steam

London, Greenwich, UK, September 2013



IAPWS-BIPM Workshops on

- Seawater salinity (R. Pawlowicz)
- Seawater pH (P. Spitzer)
- Relative Humidity (O. Hellmuth)



Joint IAPWS-BIPM Activities are coordinated by JCS

(Successor of SCOR/IAPSO WG 127)

Joint Committee on the Properties of Seawater (JCS)

The Joint Committee on the Properties of Seawater is a permanent IAPWS/SCOR/IAPSO joint committee which is responsible for maintaining and improving the recent seawater standard (TEOS-10), and for developing the cooperation with the BIPM and the WMO. In particular, the development of new definitions and measurement procedures for seawater salinity, seawater pH and relative humidity of air, traceable to the SI and thus ensuring measurement comparability over climatological time scales of decades or centuries, are being pursued by this joint committee.

Ocean Sci., 8, 161–174, 2012
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doi:10.5194/os-8-161-2012
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Ocean Science

Preface

An historical perspective on the development of the Thermodynamic Equation of Seawater – 2010

R. Pawlowicz¹, T. McDougall², R. Feistel³, and R. Tailleux⁴

<http://www.teos-10.org/JCS.htm>

Review

Metrological challenges for measurements of key climatological observables: oceanic salinity and pH, and atmospheric humidity. Part 1: overview

R Feistel¹, R Wielgosz², S A Bell³, M F Camões⁴, J R Cooper⁵, P Dexter⁶, A G Dickson⁷, P Fiscaro⁸, A H Harvey⁹, M Heinonen¹⁰, O Hellmuth¹¹, H-J Kretzschmar¹², J W Lovell-Smith¹³, T J McDougall¹⁴, R Pawlowicz¹⁵, P Ridout¹⁶, S Seitz¹⁷, P Spitzer¹⁷, D Stoica⁸ and H Wolf¹⁷

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Seawater pH

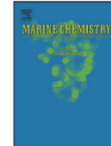
Marine Chemistry 126 (2011) 89–96



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journal homepage: www.elsevier.com/locate/marchem



pH of seawater

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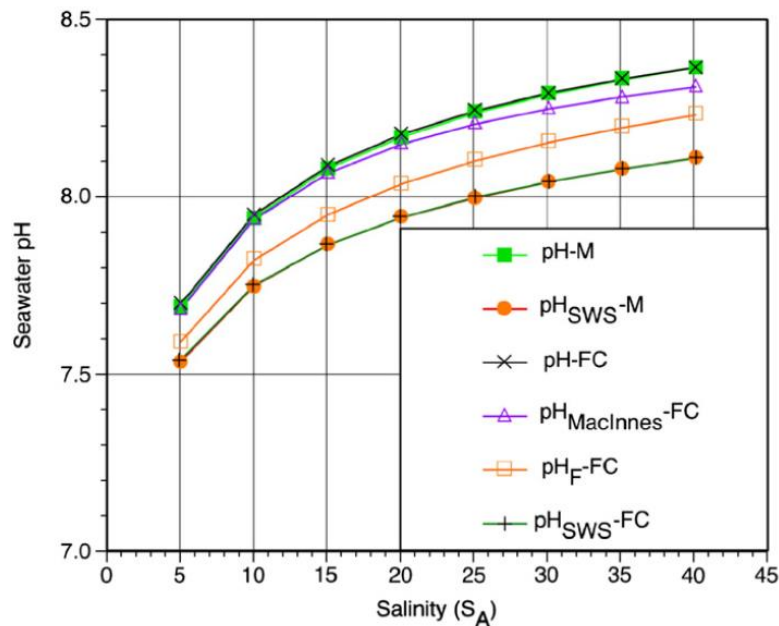


Fig. 2. Model-calculated pH values for seawater (molal concentrations, m) based on the FREZCHEM model (FC) compared to the Miami model (M). $T = 25^\circ\text{C}$, $f\text{CO}_2 = 3.33\text{E-}4$ atm.

- Proper seawater pH: Activity of H^+ ion
- Single-ion activity is not measurable
- Ion-activity equation not available for seawater
- Inconsistent practical proxies

Aim:

Pitzer equation for indicator dye

Relative Humidity, RH

- There are many RH definitions, but no SI definition yet

Metrologia 53 (2016) R40

Review

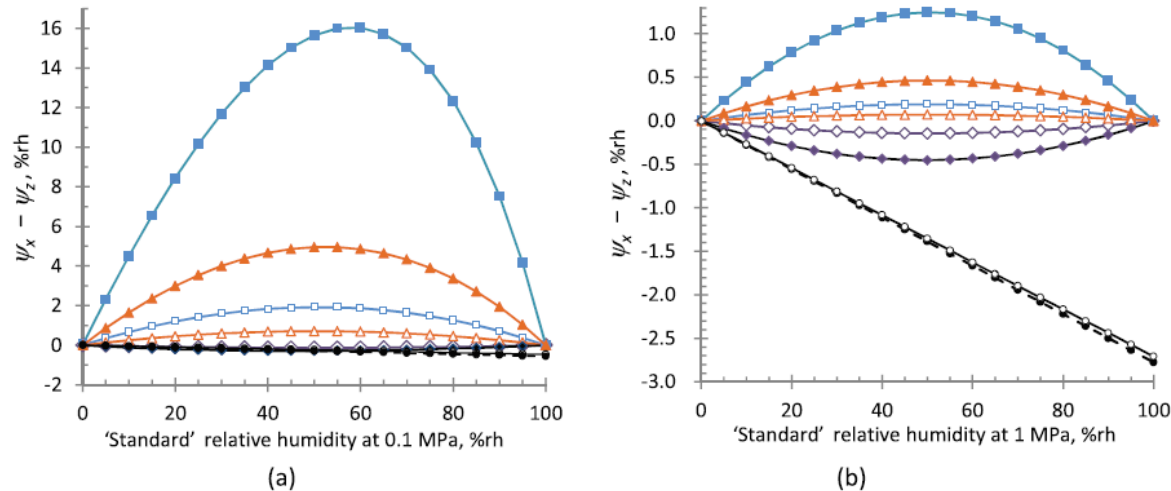


Figure 4. Differences between the standard definition ψ_x and four non-standard definitions at 40 °C (hollow symbols) and 80 °C (filled symbols) for pressures $p = 0.1$ MPa (a) and $p = 1$ MPa (b). Three non-standard definitions are of the form ψ_z , where the humidity quantity z is the mixing ratio, r (squares), the specific humidity, q (triangles), and the fugacity, f_v (diamonds). The fourth non-standard definition is ψ_{IUPAC} (circles). For each value of $\psi_x(T, p)$, x and x^{sat} are calculated and substituted into equation (20), which is rearranged to give each of the differences, $\psi_x - \psi_z$.

Preferred option:

Relative fugacity defined by IAPWS equation



J W Lovell-Smith et al. (2016): Metrological challenges for measurements of key climatological observables. Part 4: atmospheric relative humidity. Metrologia 53, R40–R59, doi:10.1088/0026-1394/53/1/R40

De-facto standard RH definition of WMO, ASHRAE, etc:

$$\psi_x(x, T, p) = \frac{x}{x^{\text{sat}}} = \frac{p_v(x, T, p)}{p_v(x^{\text{sat}}, T, p)}$$

Relative Humidity

Substitute x , p_v by their „real-gas equivalents“:

$$\psi_f(x, T, p) = \frac{a}{a^{\text{sat}}} = \frac{f_v(x, T, p)}{f_v(x^{\text{sat}}, T, p)}$$

Relative Fugacity

Define activity reference state μ_0 by the saturation state:

$$a(x^{\text{sat}}, T, p) = 1$$

Saturation State

$$RT \ln \psi_f(x, T, p) = RT \ln a_v^{\text{AV}}(x, T, p) = \mu_v^{\text{AV}}(x, T, p) - \mu_0(T, p)$$

Available from TEOS-10

„Steam Engine“ Climate



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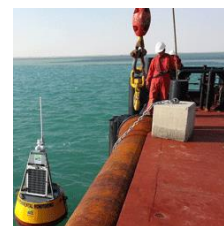
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Outlook:

The standing

SCOR/IAPSO/IAPWS Joint Committee on Properties of Seawater:

- Founded in 2012 in Boulder Co., USA
- Established in 2013 in Greenwich, UK
- Cooperation with BIPM and WMO
- SI-Definition of Seawater Salinity
- SI-Definition of Relative Humidity / Fugacity
- SI-Definition of Seawater pH

IAPWS/JCS will meet in Prague www.icpws2018.com



<http://www.teos-10.org/JCS.htm>

Thank you

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Discussion started: 7 March 2018
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Ocean Science
Discussions



Thermodynamic Properties of Seawater, Ice and Humid Air: TEOS-10, Before and Beyond

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