

Thermodynamics of Water, Vapour, Ice and Seawater

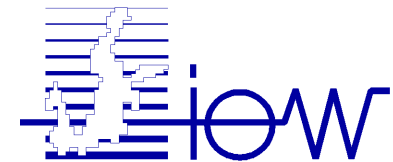


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1980, Sidney, BC



Jim Crease (retired), Werner Kröbel (deceased 6 Sep 2001), Tim M. Dauphinee (retired ?), Fred Culkin (retired but still active), Charlie Ross (retired), Edward Lyn Lewis (retired ?), Joris Gieskes (retired), Selim Morcos (active), Alain Poisson (active), Oleg I. Mamayev (deceased 28 Aug 1994), Frank J. Millero (active), Nick P. Fofonoff (deceased 18 Dec 2003), Ron G. Perkin (retired but still active), Fred Fisher (deceased), Maurice Ménaché (deceased)



SCOR Electronic Newsletter #4
October 2005

From the group of six proposals, **two new WGs were approved for a start in 2006:**

- **Thermodynamics and Equation of State of Seawater** (chair: Trevor McDougall, Australia)

This group will examine the results of recent research in ocean thermodynamics to

- **recommend a change to the internationally recommended algorithms for evaluating density and related quantities (including enthalpy, entropy and potential temperature).**
- take into account the reformulation of the **International Temperature Scale (ITS-90).**
- examine the most accurate recent knowledge of the **freezing temperature of seawater**, the **calculation of dissolved oxygen**, and the behavior of **seawater at high salinity.**
- examine the feasibility of using simple functions of three-dimensional space to account for the **effects of the spatially varying concentrations of alkalinity, total carbon dioxide, calcium and silica** on the determination of density in the ocean.

Reggio di Calabria, May 2007



G.M. Marion, RF, T.J. McDougall, B.A. King , C.-T. A. Chen, D.R. Jackett, D.G. Wright, P. Spitzer, F.J. Millero

Thermodynamics of Seawater

EOS-80 (Unesco / JPOTS 1980)

Density $\rho = \rho(S, t, p)$

Heat Capacity $c_P = c_P(S, t, p)$

Sound Speed $U = U(S, t, p)$

Freezing Point $t_f = t_f(S, p)$

Temperature: IPTS-68

Salinity: PSS-78

JPOTS = Joint Panel on Oceanographic
Tables and Standards

SCOR/IAPSO WG 127 Liaison with IAPWS

Seawater: IAPWS 2008 ?
SCOR / IAPSO 2008 ?

$$g = g^{\text{IAPWS}}(t, p) + g^{\text{S}}(S, t, p)$$

Temperature: ITS-90

Salinity: RCSS-08

Fluid Water: IAPWS-95

Ice Ih: IAPWS-06

IAPSO = International Association for
the Physical Sciences of the Oceans

SCOR = Scientific Committee on
Oceanic Research

15th International Conference on the Properties of Water and Steam

Water, Steam, and Aqueous Solutions

Advances in Science and Technology for Power Generation



September 8 - 11, 2008

Berlin, Germany

<http://www.icpws15.de/>



The International Association for the Properties of Water and Steam
Fredericia, Denmark
September 1996

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

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This release replaces the corresponding release of 1984 and contains 18 numbered pages.

This release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its Meeting in Fredericia, Denmark, 8-14 September 1996, for issue by its Secretariat. The members of IAPWS are Argentina, Canada, Czech Republic, Denmark, Germany, France, Italy, Japan, Russia, the United Kingdom, and the United States of America.

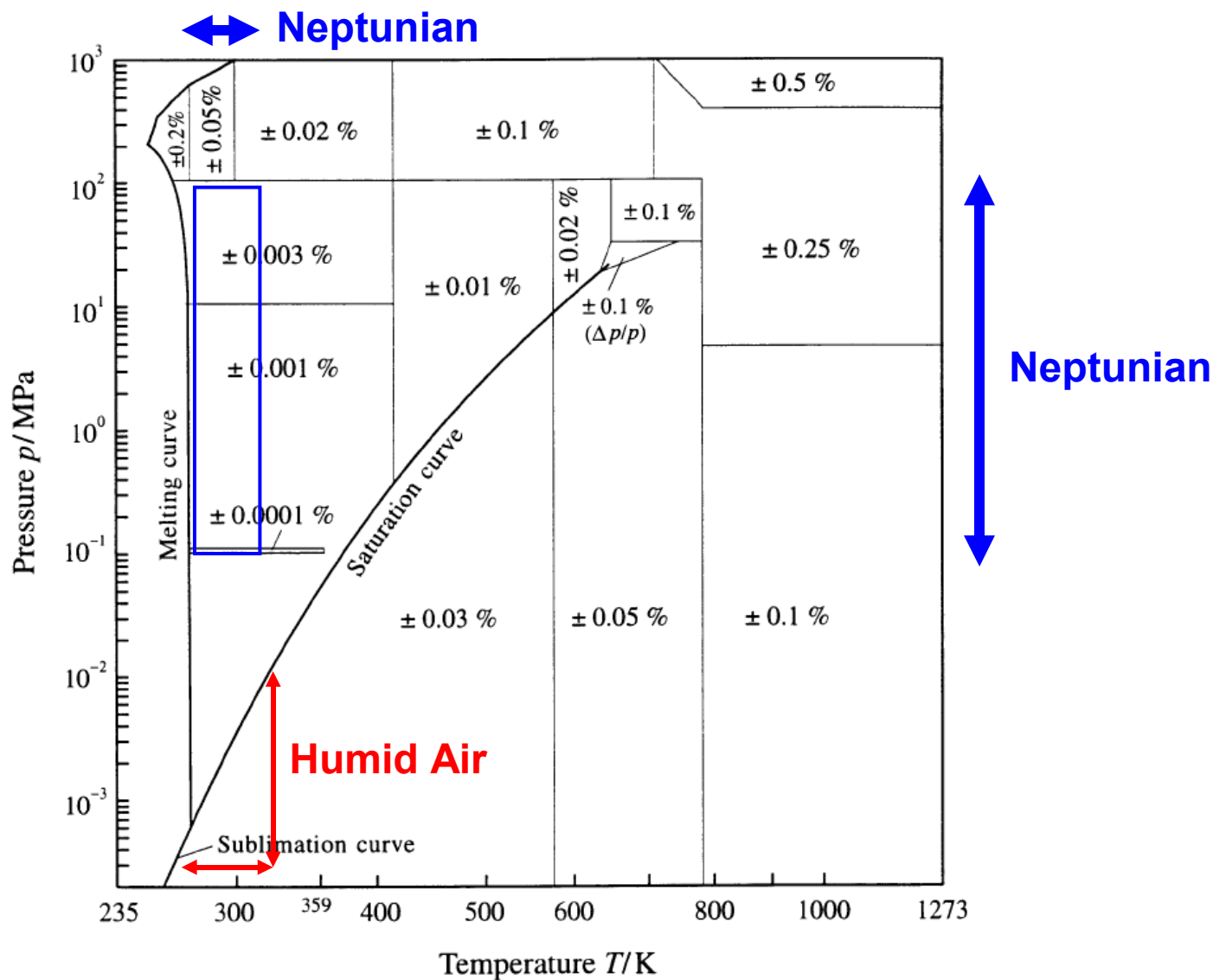


Fig. 1. Uncertainties in density, $\Delta\rho/\rho$, estimated for Eq. (4). In the enlarged critical region (triangle), the uncertainty is given as percentage uncertainty in pressure, $\Delta p/p$. This region is bordered by the two isochores 527 kg m^{-3} and 144 kg m^{-3} and by the 30 MPa isobar.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



The International Association for the Properties of Water and Steam

Witney, UK
September 2006

Release on an Equation of State for H₂O Ice Ih

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This release contains 12 pages, including this cover page.

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Gibbs Function of Ice Ih

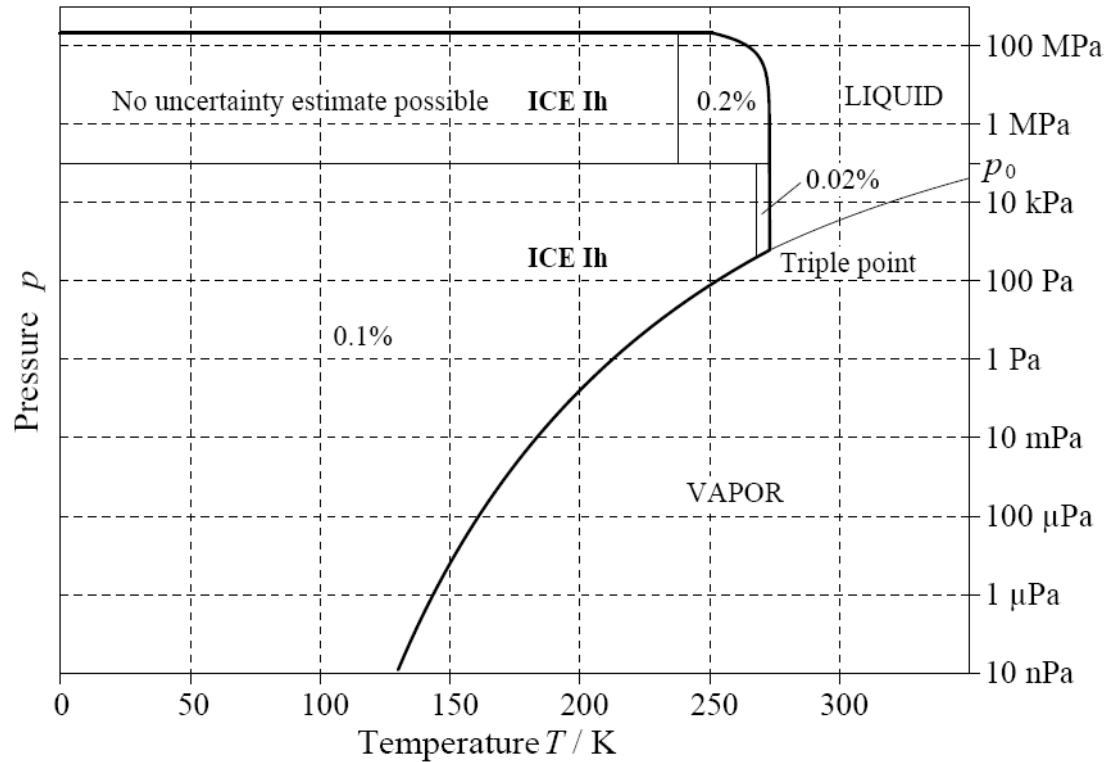
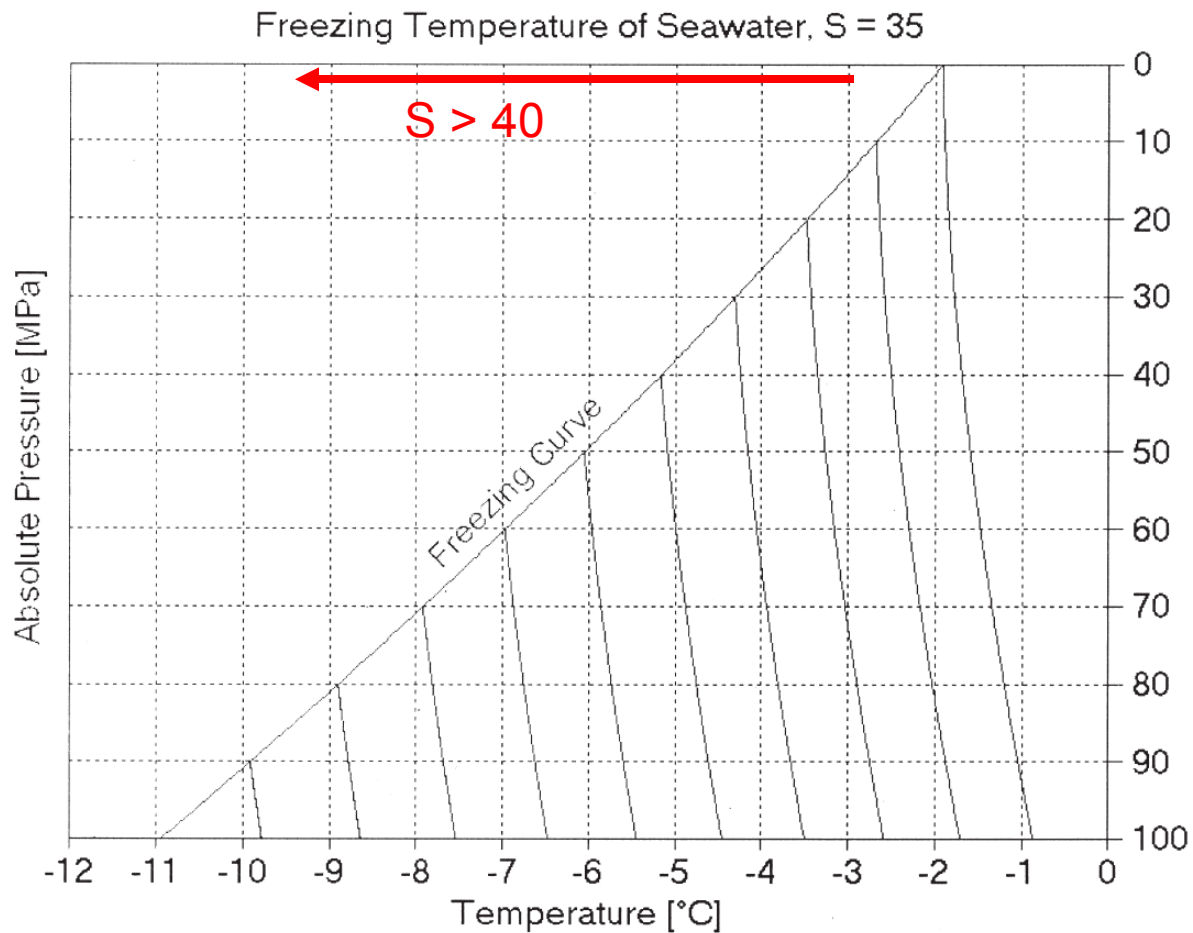


Fig. 1 Relative combined standard uncertainty of ice density, $u_c(\rho)/\rho$, Table 5, estimated for different regions of the T - p space. No experimental high-pressure data are available at low temperatures. This figure also illustrates the range of validity of the equation of state, Eq. (1).

High-pressure thermodynamic Gibbs functions of ice and sea ice

by Rainer Feistel¹ and Wolfgang Wagner²



Composition of Standard Seawater & Reference-Composition Salinity Scale

Submitted to Deep-Sea Research, 2007

F.J. Millero, RSMAS, University of Miami, USA

R. Feistel, Baltic Sea Research Institute, Warnemünde, GER

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Reasons for Reference Salinity – WG 127

Practical Salinity S on the PSS-78 scale is **separate from the system of SI units**. Reference Salinity can be expressed in the unit (g kg^{-1}), as a measure of Absolute Salinity.

The **freshwater mass fraction of seawater is not $(1 - 0.001 S)$** . Rather, it is $(1 - S_A)$, where S_A is the Absolute Salinity, defined as the mass fraction of dissolved material in seawater. The values of S_A (g kg^{-1}) and S are known to differ by about 0.5%.

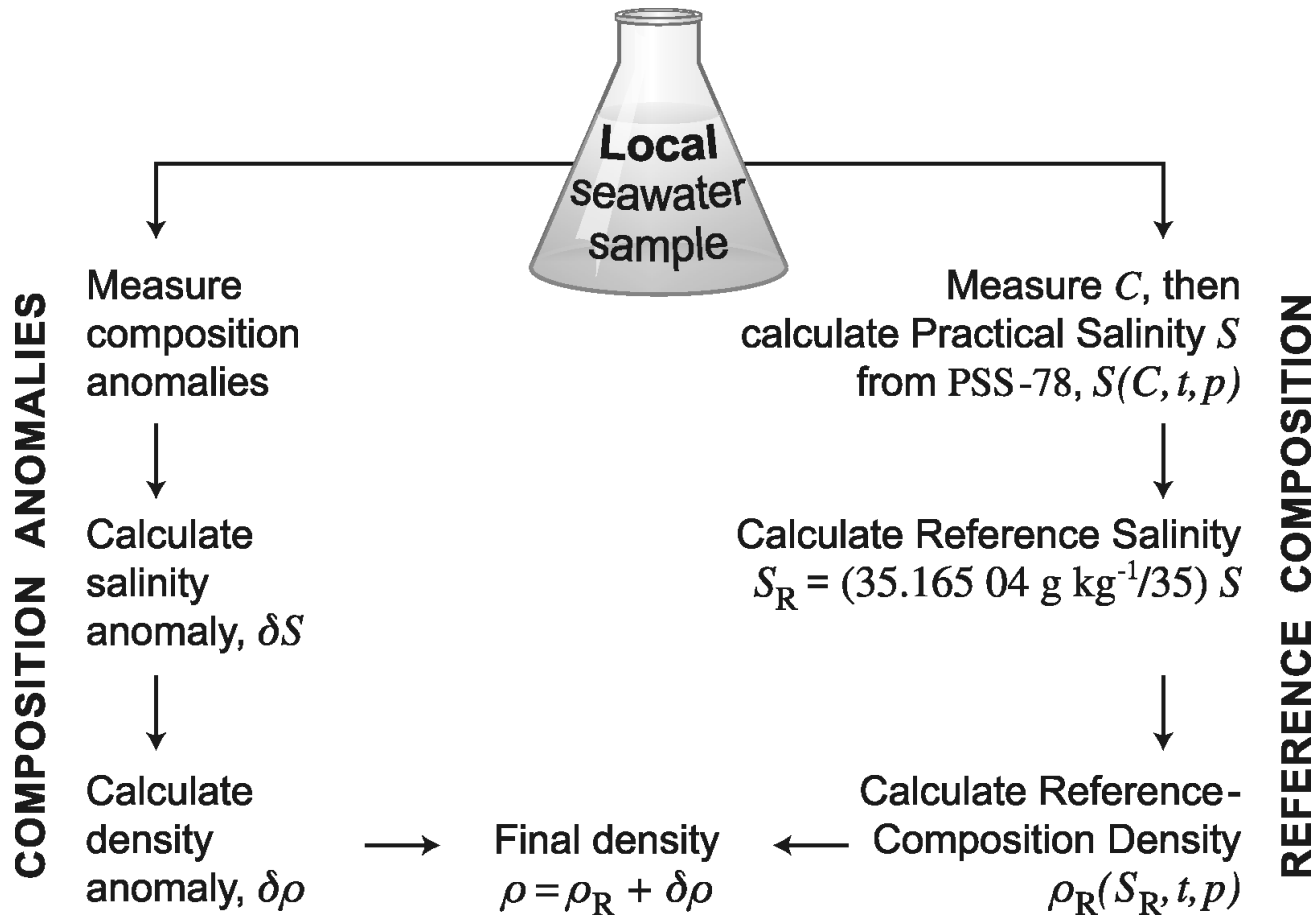
PSS-78 is **limited to the salinity range 2 to 42**. For a smooth crossover on one side to pure water, and on the other side to concentrated brines up to saturation, salinities beyond these limits need to be defined.

The Debye-Hückel limiting laws of seawater behavior at low salinities, e.g. the Gibbs function of seawater, require a **chemical composition model**.

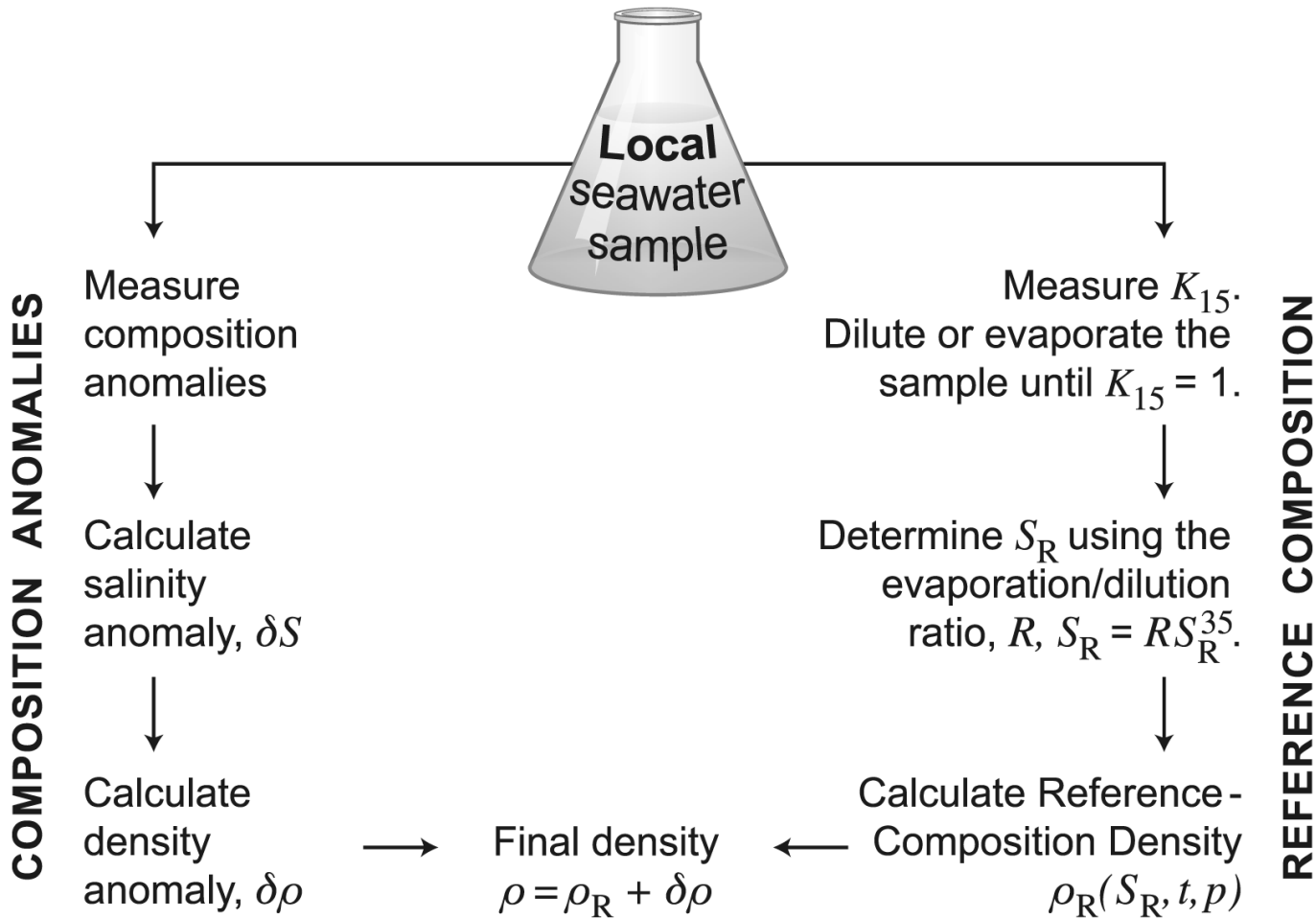
The next largest improvement in the equation of state of seawater will come from incorporating the **variation in the composition of seawater**.

Stoichiometric anomalies can be specified accurately relative to Reference Salinity with its known salt composition, but only uncertainly with respect to IAPSO Standard Seawater with unknown composition.

Practical Definition of Reference Salinity



Theoretical Definition of Reference Salinity



Definition 1 – “KCl-normalized seawater”

The term *KCl-normalized seawater* is used to describe any seawater sample that has the same specific electric conductivity as a solution of potassium chloride (KCl) in pure water with the KCl mass fraction of $32.4356 \text{ g kg}^{-1}$ when both are at the ITS-90 temperature $t = 14.996 \text{ }^\circ\text{C}$ and one standard atmosphere pressure, $P = 101325 \text{ Pa}$.

KCl refers to the normal isotopic abundances of potassium and chlorine as described by the International Union of Pure and Applied Chemistry (IUPAC 2005).

Pure water is taken here as Vienna Standard Mean Ocean Water, VSMOW, as described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS 2001).

Definition 5 – “Reference-Composition Salinity”, S_R

a) The *Reference-Composition Salinity of pure water* is defined to be zero. Pure water is meant here as Vienna Standard Mean Ocean Water, VSMOW, as described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS 2001).

b) The *Reference-Composition Salinity of normalized Reference Seawater* is defined to be exactly $35.165\,04\text{ g kg}^{-1}$.

c) The *Reference-Composition Salinity* is defined to be conservative during mixing. If a seawater sample of mass m_1 and Reference-Composition Salinity S_1 is mixed with another seawater sample of mass m_2 and Reference-Composition Salinity S_2 , the final Reference-Composition Salinity S_{12} of this sample is

$$S_{12} = \frac{m_1 S_1 + m_2 S_2}{m_1 + m_2}$$

Negative values of and corresponding to the removal of seawater with the appropriate salinity are permitted, so long as . In particular, if $S_2 = 0$ (pure water) and m_2 is chosen to normalize the seawater sample, then $S_{12} = 35.165\,04\text{ g kg}^{-1}$ and the original Reference-Composition Salinity of sample 1 is given by

$$S_1 = [1 + (m_2 / m_1)] \times 35.16504\text{ g kg}^{-1}$$

d) The *Reference-Composition Salinity of a seawater sample at given temperature and pressure* is equal to the Reference-Composition Salinity of the same sample at another temperature and pressure when the transition process is conducted without exchange of matter, in particular, without evaporation, precipitation or degassing of substance from the solution.

Definition 3 – “Reference Composition”

The *Reference Composition* of the substance dissolved in seawater, called *sea salt*, is defined by the list of solutes and their mole fractions, X_i , as given in columns 1 and 2 of **Table 4**.

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
Si 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



DRAFT – August 29., 2007

The International Association for the Properties of Water and Steam

Luzern, Switzerland

August 2007

Release on the IAPWS Formulation for the Thermodynamic Properties of Seawater

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This release contains 15 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 Luzern, Switzerland, 26-31 August, 2007, for issue by its Secretariat. The members of IAPWS are: Argentina and Brazil, Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Italy, Japan, Russia, and the United States of America.

In this release, including the title, the term seawater is used to represent the description *IAPWS Standard Seawater* [1]. The solute of seawater is referred to as sea salt, the solvent as H_2O . The equation of state for seawater provided in this release is a fundamental equation for the Gibbs energy as a function of salinity, temperature and pressure, relative to the Gibbs energy of H_2O ; details of the equation can be found in the articles "A Gibbs function for

Parts of the Gibbs Function of Seawater

Gibbs function: $g(S, t, p) = g^S(S, t, p) + g^W(t, p)$

IAPWS-95

Saline Part:

$$g^S(S, t, p) = g^S(S, t, 0) + \int_0^p v^S(S, t, p') dp'$$

$g(S, t, p)$ 2008

$S = 0 - 120$ g/kg

$T = -6 - 80$ °C

$p = 101325$ Pa

$g(S, t, p)$ 2003

$S = 0 - 42$ g/kg

$T = -2 - 40$ °C

$p = 0 - 100$ MPa

Data Used for the 2008 Gibbs function

Source	Quantity	S 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/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/Kester (1974)	t_f	4 - 40	-2 - 0	32	3	2.0	J kg ⁻¹	SS
Feistel/Marion (2007)	t_f	5 - 110	-7 - 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	g_{LL}	35	-5 - 95	21	1	0.09	J kg ⁻¹	RS
total		0 - 117	-7 - 95	602				

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

Data Used for the 2003 Gibbs function

Source	Quantity	S 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/Ghadoumi (1993)	ρ	34 - 50	15 - 30	0	10	11.3	ppm	SS
Chen/Millero (1976)	ρ	5 - 40	0 - 40	0 - 100	10	11.0	ppm	SS
Bradshaw/Schleicher (1970)	ρ^s	30 - 40	-2 - 30	1 - 100	4	2.6	ppm	SS
Caldwell (1978)	α	10 - 30	-6 - 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 - 50	-6 - 40	0 - 100				

Seawater: OS: Oregon (Pacific), SS: Standard (Atlantic)



IAPWS Certified Research Need – ICRN Thermophysical Properties of Seawater

(to be issued in 2008)

The Range of Properties Required

Salinity: between pure water and the saturation concentration
(typically more than 100 g/kg),

Temperature: from the freezing point to the boiling point, or to 680 K

Pressure: from 0 to 100 MPa, corresponding to about 10,000 m water depth.

Ranges include the conditions met in technical systems like desalination plants or the cooling systems of power stations.

Gibbs Function $g(S,t,p)$ for any Composition Model



Available online at www.sciencedirect.com



Progress in Oceanography 74 (2007) 515–539

Progress in
Oceanography

www.elsevier.com/locate/pocean

A Gibbs–Pitzer function for high-salinity seawater thermodynamics

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Planck's Ideal Solution Theory

$$g(S,t,p) = g^{\text{W}}(t,p) + S\Gamma(t,p) + N_S SkT \left\{ \ln \frac{S}{1 - \xi S} + \psi(S,t,p) \right\}$$

Pure Water

Molar Volumes and Entropies

Pitzer Equations

Gibbs-Duhem Equation

Gibbs Function $G(\mathbf{N}, T, P) = \sum_{a=0}^X N_a \mu_a(\mathbf{N}, T, P)$

Fundamental Differential $dG(\mathbf{N}, T, P) = \sum_{a=0}^X \mu_a dN_a + VdP - SdT$

Gibbs-Duhem Equation $\sum_{a=0}^X N_a d\mu_a(\mathbf{N}, T, P) = VdP - SdT$

Bjerrum Relation $d[m(1 - \phi)] + m d \ln \gamma = 0$

Integral: **Activity Potential** $\psi(m, T, P) = 1 - \phi + \ln \gamma$

Derivatives

$$\phi - 1 = m \left(\frac{\partial \psi}{\partial m} \right)_{\mathbf{x}, T, P} = I \left(\frac{\partial \psi}{\partial I} \right)_{\mathbf{x}, T, P} = S(1 - \xi S) \left(\frac{\partial \psi}{\partial S} \right)_{\mathbf{x}, T, P}$$

$$\ln \gamma = \left(\frac{\partial (m\psi)}{\partial m} \right)_{\mathbf{x}, T, P} = \left(\frac{\partial (I\psi)}{\partial I} \right)_{\mathbf{x}, T, P} = (1 - \xi S)^2 \left(\frac{\partial [S\psi / (1 - \xi S)]}{\partial S} \right)_{\mathbf{x}, T, P}$$

Salinities up to 110 g/kg:

The Chemist's Approach to Seawater

Pitzer Equations:

Osmotic Coefficient,
Water

$$(\phi - 1) = \frac{2}{\sum m_i} \left\{ \frac{-A_\phi I^{3/2}}{1 + b I^{1/2}} + \sum \sum m_c m_a (B_{ca}^\phi + Z C_{ca}) + \sum \sum m_c m_{c'} (\Phi_{cc'}^\phi + \sum m_a \Psi_{cc'a}) \right. \\ \left. + \sum \sum m_a m_{a'} (\Phi_{aa'}^\phi + \sum m_c \Psi_{caa'}) + \sum \sum m_n m_c \lambda_{nc} + \sum \sum m_n m_a \lambda_{na} \right. \\ \left. + \sum \sum \sum m_n m_c m_a \xi_{n,c,a} \right\}$$

Activity Coefficient,
Cation "M"

$$\ln(\gamma_M) = z_M^2 F + \sum m_a (2B_{Ma} + ZC_{Ma}) + \sum m_c (2\Phi_{Mc} + \sum m_a \Psi_{Mca}) \\ + \sum \sum m_a m_{a'} \Psi_{Maa'} + z_M \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nM} + \sum \sum m_n m_a \xi_{nMa}$$

Activity Coefficient,
Anion "X"

$$\ln(\gamma_X) = z_X^2 F + \sum m_c (2B_{cX} + ZC_{cX}) + \sum m_a (2\Phi_{Xa} + \sum m_c \Psi_{cXa}) \\ + \sum \sum m_c m_{c'} \Psi_{cc'X} + |z_X| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nX} + \sum \sum m_n m_c \xi_{ncX}$$

Activity Coefficient,
Neutral Particle "N"

$$\ln(\gamma_N) = \sum m_c (2\lambda_{Nc}) + \sum m_a (2\lambda_{Na}) + \sum \sum m_c m_a \xi_{ca}$$

Marion, G. M., Farren, R. E. & Komrowski, A. J.: Alternative pathways for seawater freezing. Cold Regions Science and Technology, 29 (1999) 259-266

Andrea Koschinsky, on r/v METEOR, April - June 2006, registered 407 °C at a hydrothermal vent at 3000 m as the highest temperature ever measured at the ocean bottom.



Fluid sampling and temperature measurement at 3000 m water depth and 407 °C with deep-sea robot QUEST 5 at 5 °S at the Mid-Atlantic Ridge (Copyright MARUM, University of Bremen)

“407 °C at 3000 m depth marks the critical temperature, where water is no longer a fluid but reaches the state of “critical vapor“ cruise leader Koschinsky says.

“This special state of aggregation differs markedly from liquid water in the way it leaches materials such as metals from the bedrock. The result of the process are super-hot solutions of highly unusual composition.“

Thank You