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A Gibbs function for seawater thermodynamics for -6 to 80 °C and salinity up to 120 g kg $^{-1}$

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ABSTRACT

The specific Gibbs energy of seawater is determined from experimental data of heat capacities, freezing points, vapour pressures and mixing heats at atmospheric pressure in the range -6 to 80 °C in temperature and 0 – 120 g kg $^{-1}$ in absolute salinity. Combined with the pure-water properties available from the 1996 Release of the International Association for the Properties of Water and Steam (IAPWS-95), and the densities from the 2003 Gibbs function of seawater, a new saline part of the Gibbs function is developed for seawater that has an extended range of validity including elevated temperatures and salinities. In conjunction with the IAPWS 2006 Release on ice, the correct description of concentrated brines by the new formulations permits an accurate evaluation of sea ice properties down to salinity saturation temperatures. The new Gibbs function is expressed in terms of the temperature scale ITS-90. Its input variable for the concentration is absolute salinity, available from the new Reference-Composition Salinity Scale of 2008.

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1. Introduction

During the three decades since the introduction of the Practical Salinity Scale, PSS-78, and the International Equation of State of Seawater, EOS-80 (UNESCO, 1981), demand has grown for more accurate equations, additional available properties, extended ranges of validity and rigorous consistency with other international standards. Over this period of time, speed and memory of standard computers have increased enormously, at least by a factor of 1000, permitting more complex algorithms to be implemented and used routinely in oceanographic practice. Simultaneously but almost without implications for the current oceanographic standards, the International Temperature Scale of 1990 (ITS-90) was introduced, new scientific formulations for the thermodynamic properties of liquid water, vapour and ice (IAPWS, 1996, 2006) were released, and fundamental physical and chemical con-

stants like the atomic weights (Wieser, 2006) have continuously improved. To cope with this development, the SCOR/IAPSO Working Group 127 on Thermodynamics and Equation of State of Seawater (WG127) was established in 2005, in parallel with a similar activity of the International Association for the Properties of Water and Steam (IAPWS), aiming at the development of an internationally recognized seawater standard, e.g. for the technical specification of industrial constructions like power stations or desalination plants.

As necessary steps towards this goal, on its meetings 2006 in Warnemünde, Germany, and 2007 in Reggio di Calabria, Italy, the WG127

- (i) developed a composition model for standard seawater, regarded as the reference composition, which permits the determination of the model's absolute salinity by the definition of the Reference-Composition Salinity Scale (Millero et al., 2008). Termed in short reference salinity, S_R , this represents the absolute salinity of IAPSO Standard Seawater within an

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Nomenclature

c	sound speed, m s^{-1}	R	molar gas constant, $\text{J K}^{-1} \text{mol}^{-1}$
C	speed of light (only in Table 13), m s^{-1}	r	electrical power ratio
c_{ij}	adjustable constants	r_{R54}	vapour pressure ratio
Cl	chlorinity, g kg^{-1}	r_D	Debye radius, nm
c^S	sound speed, saline part, m s^{-1}	S	Practical Salinity
c^W	sound speed, water part, m s^{-1}	s	specific entropy, $\text{J kg}^{-1} \text{K}^{-1}$
c_p	specific isobaric heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$	s^{lh}	specific entropy of ice lh, J kg^{-1}
c_p^S	specific isobaric heat capacity, saline part, $\text{J kg}^{-1} \text{K}^{-1}$	s^S	specific entropy, saline part, J kg^{-1}
$c_{p,0}^S$	specific isobaric heat capacity at $p = 0$, saline part, $\text{J kg}^{-1} \text{K}^{-1}$	s_0^S	specific entropy at $t = 0$ and $p = 0$, saline part, J kg^{-1}
c_p^W	specific isobaric heat capacity, water part, $\text{J kg}^{-1} \text{K}^{-1}$	s^{vap}	specific entropy of water vapour, J kg^{-1}
c_v	specific isochoric heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$	s^W	specific entropy, water part, J kg^{-1}
f	specific Helmholtz energy, J kg^{-1}	S_A	absolute salinity, g kg^{-1}
G	Gibbs energy of seawater, J	S_K	Knudsen salinity
g	specific Gibbs energy, J kg^{-1}	S_R	reference-composition salinity, g kg^{-1}
g^{lh}	specific Gibbs energy of ice lh, J kg^{-1}	S_{SO}	standard ocean absolute salinity (normal salinity), g kg^{-1}
g_{ijk}	coefficients of the Gibbs function	S_u	unit-dependent salinity constant, g kg^{-1}
g^{LL}	limiting-law part of the Gibbs function, J kg^{-1}	T	absolute temperature, ITS-90, K
$g_p, g_{T, \dots}$	partial derivatives of the Gibbs function	t	celsius temperature, ITS-90, $^{\circ}\text{C}$
g^S	saline part of the specific Gibbs energy, J kg^{-1}	T_0	celsius zero point, K
g_0^S	specific Gibbs energy at $t = 0$ and $p = 0$, saline part, J kg^{-1}	T_{48}	absolute temperature, IPTS-48, K
g_u	unit-dependent energy constant, J kg^{-1}	t_{48}	celsius temperature, IPTS-48, $^{\circ}\text{C}$
g^W	water part of the specific Gibbs energy, J kg^{-1}	T_{68}	absolute temperature, IPTS-68, K
g^{vap}	specific Gibbs energy of water vapour, J kg^{-1}	t_{68}	celsius temperature, IPTS-68, $^{\circ}\text{C}$
h	specific enthalpy, J kg^{-1}	T_{90}	absolute temperature, ITS-90, K
h_{mix}	specific mixing enthalpy, J kg^{-1}	T_{boil}	boiling temperature, K
h^S	specific enthalpy, saline part, J kg^{-1}	T_c	critical temperature, K
h^W	specific enthalpy, water part, J kg^{-1}	t_f	freezing temperature, $^{\circ}\text{C}$
h_θ	potential enthalpy, J kg^{-1}	t_{SO}	standard ocean temperature, $^{\circ}\text{C}$
k	uncertainty coverage factor,	T_t	triple-point temperature, K
k	Boltzmann constant, J K^{-1}	t_{sw}	boiling temperature of seawater, $^{\circ}\text{C}$
k_p	barodiffusion ratio, g kg^{-1}	t_u	unit-dependent temperature constant, $^{\circ}\text{C}$
m	molality, mol kg^{-1}	U	expanded uncertainty
m, m_1, m_2	sample mass, kg	u	specific internal energy, J kg^{-1}
M_S	molar mass of sea salt, g mol^{-1}	u_c	combined standard uncertainty
m_S	mass of salt, kg	u_{Cl}	conversion factor of chlorinity to reference salinity
m_W	mass of water, kg	u_{PS}	conversion factor of practical to reference salinity, g kg^{-1}
n_0^1, n_0^2	adjustable coefficients of IAPWS-95	u^W	specific internal energy, water part, J kg^{-1}
N_A	Avogadro number, mol^{-1}	v	specific volume, $\text{m}^3 \text{kg}^{-1}$
N_S	number of salt particles per gram of sea salt, g^{-1}	v^{lh}	specific volume of ice lh, $\text{m}^3 \text{kg}^{-1}$
P	absolute pressure, Pa	v^S	specific volume, saline part, $\text{m}^3 \text{kg}^{-1}$
p	gauge pressure, Pa	v^W	specific volume, water part, $\text{m}^3 \text{kg}^{-1}$
P_0	standard atmospheric pressure (normal pressure), Pa	v^{vap}	specific volume of water vapour, $\text{m}^3 \text{kg}^{-1}$
P_c	critical pressure, Pa	W	electrical energy, J
P_t	triple-point pressure, Pa	w_1, w_2	sample mass fraction
p_r	reference pressure, Pa	x	dimensionless absolute salinity root
p_{SO}	standard ocean surface pressure, Pa	y	dimensionless celsius temperature
p_u	unit-dependent pressure constant, Pa	Z	valence number
p^{vap}	absolute vapour pressure, Pa	z	dimensionless gauge pressure
p^{vap}	gauge vapour pressure, Pa	α	thermal expansion coefficient, K^{-1}
Q	mixing heat, J	ΔS	mixing salinity, g kg^{-1}
q	relative mixing enthalpy, J kg^{-1}	ϵ_0	electric constant, F m^{-1}
		ϵ^W	static dielectric constant of water
		κ_D	Debye parameter, nm^{-1}
		κ_T	isothermal compressibility, Pa^{-1}
		μ	relative chemical potential, J kg^{-1}
		μ^{lh}	chemical potential of ice lh, J kg^{-1}

μ^S	chemical potential of salt in seawater, J kg^{-1}	ρ^S	density, saline part, kg m^{-3}
μ^W	chemical potential of water in seawater, J kg^{-1}	ρ^W	density, water part, kg m^{-3}
Ω	penalty function for the least-square fit	ρ_θ^W	potential density of water, kg m^{-3}
ω	tolerance of the penalty function	ρ^{vap}	density of water vapour, kg m^{-3}
π	number Pi, 3.1415...	θ	potential temperature, $^\circ\text{C}$
ρ	density, kg m^{-3}	ϕ	osmotic coefficient

estimated uncertainty of 0.007 g kg^{-1} and has well-defined relations to Practical Salinity and chlorinity. This concept allows the intended new seawater formulation to be expressed in standard SI units for absolute salinity rather than in Practical Salinity units which are almost exclusively used in oceanography, but are not used in other fields. It further supports the full-range crossover from zero to saturation concentrations in models and measurements, beyond the limits where PSS-78 is defined.

- (ii) Adopted the Gibbs function formalism (Fofonoff, 1962; Feistel, 1993, 2003; Feistel and Hagen, 1995) as a suitable theoretical framework for the new seawater formulation. Mathematically, as a thermodynamic potential (Alberty, 2001), the Gibbs function permits the consistent computation of all thermodynamic properties of seawater from a single expression (Tables 17 and 18). This naturally includes several quantities like entropy or enthalpy not available from EOS-80.
- (iii) Adopted the IAPWS Releases 1996 (henceforth referred to as IAPWS-95) and 2006 (IAPWS-06) on fluid water and ice as the exact pure-water limits for seawater and sea ice properties in the case of vanishing salinity.
- (iv) Proposed the extension of the ranges of validity in temperature and salinity beyond those of EOS-80, which depend on the availability of further reliable and accurate seawater data.

Using this approach, several weaknesses of the EOS-80 formulation can be overcome (Feistel, 2003), regarding

(A) Agreement with experiments:

- (i) EOS-80 does not properly describe high-pressure sound speed as derived from deep-sea travel times (Spiesberger and Metzger, 1991; Dushaw et al., 1993; Millero and Li, 1994; Meinen and Watts, 1997).
- (ii) Due to (i), there is evidently a potential conflict between abyssal travel-time measurements and EOS-80 high-pressure densities, which are considered consistent with EOS-80 sound speed.
- (iii) EOS-80 does not accurately represent the temperatures of maximum density determined experimentally, especially for brackish waters under pressure (Caldwell, 1978; Siedler and Peters, 1986).
- (iv) The pressure coefficient of the EOS-80 freezing temperature differs from the most accurate

experiments, significantly exceeding their uncertainty (Ginnings and Corruccini, 1947; Feistel and Wagner, 2005, 2006).

(B) Consistency with international standards:

- (i) EOS-80 is not expressed in terms of the international temperature scale ITS-90 (Blanke, 1989; Preston-Thomas, 1990; Saunders, 1990).
- (ii) At zero salinity, EOS-80 shows systematic deviations from the international pure-water standard IAPWS-95 (Wagner and Pruß, 2002), especially in compressibility, thermal expansion, and sound speed.
- (iii) EOS-80 is derived from seawater measurements relative to or calibrated with fresh-water properties which are partly obsolete with respect to the new pure water standard IAPWS-95.
- (iv) The range of validity for EOS-80 does not include the triple point of water which is a standard reference point for thermodynamic descriptions of water.

(C) Internal consistency of the formulation:

- (i) EOS-80 is redundant and contradictory, as certain thermodynamic properties like heat capacity can be computed by combining other equations of EOS-80, sometimes leading to significantly different results, especially near the density maximum.
- (ii) EOS-80 obeys thermodynamic cross-relations (Maxwell relations) only approximately but not identically.
- (iii) Freezing-point temperatures are valid for air-saturated water, while other EOS-80 formulas are defined for air-free water, thus causing systematic offsets.

(D) Completeness of the formulation:

- (i) EOS-80 does not provide specific enthalpy which is required for the hydrodynamic energy balance by means of the enthalpy flux (Landau and Lifschitz, 1974; Bacon and Fofonoff, 1996; Warren, 1999) or the Bernoulli function (Gill, 1982; Saunders, 1995). Specific enthalpy is further necessary for the calculation of mixing heat (Fofonoff, 1962) or of conservative quantities like potential enthalpy (McDougall, 2003).
- (ii) EOS-80 does not provide specific entropy as an unambiguous alternative for potential temperature (Feistel and Hagen, 1994). Inclusion of specific entropy would, for example, allow for an effective and accurate computation of potential temperature and potential density (Bradshaw, 1978; Feistel, 1993), especially in numerical ocean models (McDougall et al., 2003; Jackett et al., 2006).

- (iii) EOS-80 does not provide specific internal energy, which like enthalpy is required for proper energy balances, and e.g. elucidates the changing thermal water and seawater properties when being compressed (McDougall and Feistel, 2003).
- (iv) EOS-80 does not provide chemical potentials which allow the computation of properties of vapour pressure or osmotic pressure (Millero and Leung, 1976), or properties of sea ice (Feistel and Hagen, 1998), or as indicators for actively mixing oceanic layers (Feistel and Hagen, 1994).
- (v) Practical Salinity S used as the concentration variable for EOS-80 is not rigorously conservative, deviates by almost 0.5% from absolute salinity in g/kg, and is undefined for $S < 2$ in coastal lagoons or for $S > 42$ found in evaporating seas or in sea ice below -3°C (Mamayev et al., 1991; Feistel and Marion, 2007; Millero et al., 2008).
- (vi) Properties like osmotic or activity coefficients are specified in terms of molality, derived from absolute salinity (Millero and Leung, 1976; Feistel and Marion, 2007) which remains undefined in the EOS-80 standard.
- (vii) EOS-80 freezing-point temperatures are valid up to pressures of 5 MPa (500 dbar), which is insufficient for extreme polar systems like Lake Vostok (Siebert et al., 2001).

Here, EOS-80 refers to four correlation equations, providing separate algorithms for the density, heat capacity, sound speed, and the freezing temperature of seawater (Fofonoff and Millard, 1983).

In this paper, a new Gibbs function is developed and the underlying mathematical formalism is described, according to the recommendation of WG127. This function resolves the above issues; regarding A- (iv), C- (iii) and D- (vii), the Gibbs function of seawater must be used in conjunction with a consistently formulated Gibbs potential of ice (Feistel and Wagner, 2005, 2006; Feistel et al., 2005; IAPWS, 2006). The consistency requirements are reconsidered in more detail in Section 6.1, and recently improved coefficients are provided by Feistel et al. (2008c).

As is well known from standard textbooks on thermodynamics (e.g. Landau and Lifschitz, 1966; Alberty, 2001), if a fundamental equation of a system (such as the Gibbs function) is known, commonly regarded as a thermodynamic potential of that system, a complete thermodynamic representation of the system is available from this function, and a wide range of seemingly unrelated thermodynamic equilibrium properties can be calculated by appropriate differentiation and algebraic manipulation, including the so-called equation of state.

The system integrity of the new formulation is two levels higher than that of the former EOS-80. First, the individual correlation equations for particular properties of seawater are consistently combined into one single compact function, the thermodynamic potential. Second, three such independent potential functions (for fluid water, for ice, and for sea salt dissolved in water) are

combined consistently, in turn, providing not only the properties of the single phases/components, but also of their mutual combinations and transitions. Conveniently, such a family of thermodynamic potentials possesses the same three general properties as axiomatic systems. It is *consistent* (excluding the deduction of two different formulas for the same property), *independent* (preventing any formula from being deducible from other ones) and *complete* (providing a formula for every thermodynamic property).

For seawater, the preferred independent variables of formulas and algorithms constructed for the computation of properties like density or sound speed, are temperature, pressure and salinity. The proper thermodynamic potential depending on these particular natural variables is the Gibbs function (Fofonoff, 1962; Feistel, 1993; Alberty, 2001). The actual mathematical form of this potential cannot be derived from thermodynamic principles; it depends on the substance, the accuracy and the range of validity chosen to be modelled, except for some very general conditions like positive heat capacity or positive compressibility, which are related to the validity of the Second Law of thermodynamics (Landau and Lifschitz, 1966). Thus, the Gibbs function of seawater must be constructed from available experimental data and theoretical relations like the Debye–Hückel limiting law. In this construction process, the wealth of information available from various experiments is condensed into a comparatively small set of adjustable coefficients of the potential function. This information compression can be performed successfully only if the employed data sets are accurate and consistent; any systematic error in a particular data set must necessarily create intractable conflicts with other data, and usually becomes evident immediately. This is true in particular for seawater for which extremely accurate experiments were performed, e.g. for density, heat capacity or sound speed, mostly already during the 1960s and 1970s.

The Gibbs energy, G , of a seawater sample containing the mass of water, m_W , and the mass of salt, m_S , at the absolute temperature T and the absolute pressure P , can be written in the form

$$G(m_W, m_S, T, P) = m_W \mu^W + m_S \mu^S \quad (1.1)$$

with the chemical potential of water in seawater, μ^W , and of salt in seawater, μ^S , being defined by the partial derivatives

$$\mu^W = \left(\frac{\partial G}{\partial m_W} \right)_{T,P,m_S}, \quad \mu^S = \left(\frac{\partial G}{\partial m_S} \right)_{T,P,m_W} \quad (1.2)$$

Introducing absolute salinity, $S_A = m_S/(m_W+m_S)$, as the mass fraction of salt dissolved in seawater (Millero et al., 2008), the specific Gibbs energy

$$g(S_A, t, p) = \frac{G}{m_W + m_S} = \mu^W + S_A(\mu^S - \mu^W) \quad (1.3)$$

is independent of the total mass of the sample and will be used as the appropriate thermodynamic potential function for seawater in this paper. Here we have switched to Celsius temperature, t , and gauge pressure, p (relative to the standard atmospheric pressure assumed at the sea

surface, briefly the normal pressure), being the traditional measures in oceanography. The attribute “specific” in front of quantities like enthalpy, entropy, etc. will sometimes be omitted in this paper since—with very few exceptions regarding certain published experimental data—exclusively specific rather than extensive thermodynamic quantities are considered in this text.

The specific Gibbs energy, g , of seawater as a function of absolute salinity, S_A , ITS-90 temperature, t , and pressure, p , can be decomposed uniquely into the Gibbs energy of liquid pure water, g^W , and a salinity correction, g^S , the *saline part of the Gibbs energy*, in short *saline Gibbs energy*, as

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p), \quad (1.4)$$

subject to the formal condition $g^S(0, t, p) = 0$. The relations of g^W and g^S to the chemical potentials, Eqs. (1.2) and (1.3), are given in Table 19. The same splitting as in (1.4) obviously holds then for all quantities obtained from g as linear functions of its partial derivatives, like e.g. the specific volume, $v = (\partial g / \partial p)_{S_A, t}$. The pressure dependence of the second term of (1.4) can thus be separated, in turn, as an integral over the saline specific volume, $v^S = v - v^W$, as

$$g^S(S_A, t, p) = g^S(S_A, t, 0) + \int_0^p v^S(S_A, t, p') dp'. \quad (1.5)$$

A highly accurate function g^W is implicitly available from the IAPWS-95 formulation for liquid water (Wagner and Pruß, 2002; IAPWS, 1996) which covers wide ranges of temperature and pressure. The former saline Gibbs energy g^S , available from the 2003 Gibbs function of seawater (Feistel, 2003, briefly F03 further on), was only designed for Practical Salinity up to 42, temperatures -2 to 40 °C, and pressure up to 100 MPa. A recent study (Feistel and Marion, 2007) has revealed that the related saline volume v^S extrapolates surprisingly well to salinities even up to saturation concentrations (about 110 kg kg^{-1}) at temperatures below 25 °C, Fig. 8. In contrast, the corresponding osmotic coefficients computed from the F03 saline Gibbs energy at normal pressure, $g^S(S_A, t, 0)$, exhibit significant extrapolation errors. This function $g^S(S_A, t, 0)$ possesses by far the largest uncertainties at higher salinities compared to the remaining two terms, g^W and v^S , in Eqs. (1.4) and (1.5). Since accurate experimental thermal and colligative data of seawater are available for high salinities and high temperatures at normal pressure, the applicability range of the Gibbs function of seawater can be significantly expanded by a new determination of its saline Gibbs energy, $g^S(S_A, t, 0)$, exploiting those measurements.

The procedure is particularly transparent because of the polynomial structure of F03, demanding only the recomputation of some of its coefficients and leaving the rest unaltered, since analogous experimental data for v^S are not available for high salinities, temperatures and pressures. This concept is carried out in this paper, as follows:

- adopt g^W from IAPWS-95 and discuss the equations and conditions required;

- adopt v^S from F03;
- construct $g^S(S_A, t, 0)$ from seawater data at 0 – 80 °C, 0 – 120 kg kg^{-1} ;
- estimate uncertainties of the resulting combined function $g(S_A, t, p)$.

When seawater freezes, sea ice is formed, consisting of a mixture of pure-water ice with concentrated seawater, called brine. With falling temperature, the brine equilibrium salinity is increasing rapidly, exceeding a salinity of 40 kg kg^{-1} already at temperatures below -3 °C at normal pressure. Due to the latent contributions from the freezing enthalpy and the freezing volume of ice, the heat capacity and the thermal expansion coefficient of sea ice possess exceptional high values. Thermodynamically, these quantities are most accurately described by the Gibbs function method (Feistel and Hagen, 1998; Feistel and Wagner, 2005) if appropriate Gibbs functions of ice and of seawater are available for the considered ranges in salinity, temperature and pressure. The latest version of the Gibbs potential function of ice was described by Feistel and Wagner (2006) and issued as a Release of the International Association for the Properties of Water and Steam (IAPWS, 2006), covering the entire range of existence of the naturally abundant hexagonal ice (ice Ih). The latest version of the Gibbs potential of seawater (Feistel, 2003), is limited in its validity to Practical Salinity values up to 42 (up to 50 in some derived quantities). Hence, a proper Gibbs function of sea ice is currently not available for temperatures below -3 °C, i.e. for usual ambient conditions at higher latitudes.

A first attempt at constructing a Gibbs function for the full range of salinities between zero and saturation was made by Feistel and Marion (2007), based on empirical Pitzer equations for aqueous electrolyte models rather than on experimental seawater data. Substantial uncertainties occur particularly in the partial second derivatives of this Gibbs function which describe, e.g. the heat capacity, the compressibility or the thermal expansion.

The definition of the Practical Salinity Scale of 1978 (PSS-78) ends at salinity 42 (UNESCO, 1981), extended later to 50 by Poisson and Gadhoumi (1993). To overcome this limitation and to address a number of other issues concerning the definition of salinity of Standard Seawater, a new reference salinity scale has recently been proposed by the IAPSO/SCOR Working Group 127 on Thermodynamics and Equation of State of Seawater, briefly WG127 (SCOR, 2005; Millero et al., 2008). This scale estimates the absolute salinity of standard seawater in g kg^{-1} and can be used over the entire solubility range of the sea salt components. The new equation of state developed in this paper is expressed in terms of absolute salinity, using the formula symbol S_A . The numerical value of S_A in g kg^{-1} is greater than Practical Salinity by a factor of about 1.0047, see Section 2 for details.

For seawater with standard composition, absolute salinity and reference salinity are considered as entirely equivalent in this paper. Nonetheless, the Gibbs function given here is expressed in terms of absolute salinity rather than reference salinity for its possible application to

seawater with small composition anomalies. In such cases, density, as the most sensitive property in this respect, is independent of small chemical composition variations if expressed in terms of absolute salinity (Millero et al., 2008). This is no longer true if reference salinity is used as the concentration variable, computed from the conductivity of the anomalous sample.

There is a growing interest in the high-salinity properties of hot seawater, too. On the one hand, tropical estuaries like the Australian Shark Bay (Logan and Cebulsk, 1970) show salinities up to 70 g kg^{-1} , and desiccating seas like the Dead Sea or the paleo-oceanographic Mediterranean (Meijer and Krijgsman, 2005) even approach saturation concentrations. As well, the economic demand for fresh water resources and higher energy efficiency has fuelled advances in the technology of low-temperature desalination plants, operating typically at temperatures below 80°C (El-Dessouky et al., 2000; Kronenberg and Lokiez, 2001; Sidem/Entropie, 2006; Schiermeier, 2008). For these reasons, the high-salinity extension of the Gibbs function developed in this paper covers temperatures up to 80°C in its thermal and colligative properties at normal pressure. The expressions for density and its derivatives at high salinities and temperatures are the same as in F03, due to the lack of appropriate experimental data in this range. These particular extrapolations from F03 possess lower accuracies, as estimated in Section 7.

The development of a joint, consistent and very accurate international standard on the thermodynamic properties of seawater, valid over the natural and technical ranges in temperature, pressure and salinity, and including its phase equilibrium properties with ice and vapour, is jointly supported by WG127 and IAPWS. For this purpose, the formulation of three independent fundamental functions is necessary and sufficient, (i) a thermodynamic potential of fluid (i.e. liquid and gaseous) water, (ii) a thermodynamic potential of ice and (iii) a salinity correction to the potential of liquid water. The first two are already available from the IAPWS Releases 1996 and 2006, and this paper presents a formulation of the third part, planned to be adopted by IAPWS as a Release in 2008. In contrast to the Gibbs functions used for ice and seawater, fluid water is described mathematically by its Helmholtz thermodynamic potential, i.e. its specific Helmholtz energy as a function of temperature and density. The basic concepts of the related thermodynamic potential formalisms are briefly explained in Section 3. The explicit use of the numerical IAPWS-95 implementation as the pure-water reference for seawater at temperatures higher than 40°C is indispensable since standard seawater formulas show significant extrapolation errors at these temperatures in their pure-water parts. The uncertainty of IAPWS-95 densities up to 80°C at normal pressure is estimated as small as 1 ppm (Fig. 1). Since this is the first time a Gibbs function of seawater is developed explicitly in the form of a salinity correction to IAPWS-95, attention must be paid to some of its affected properties as explained in Section 4. In the future, further progress will become possible when appropriate experimental data on high-pressure properties of seawater become available.

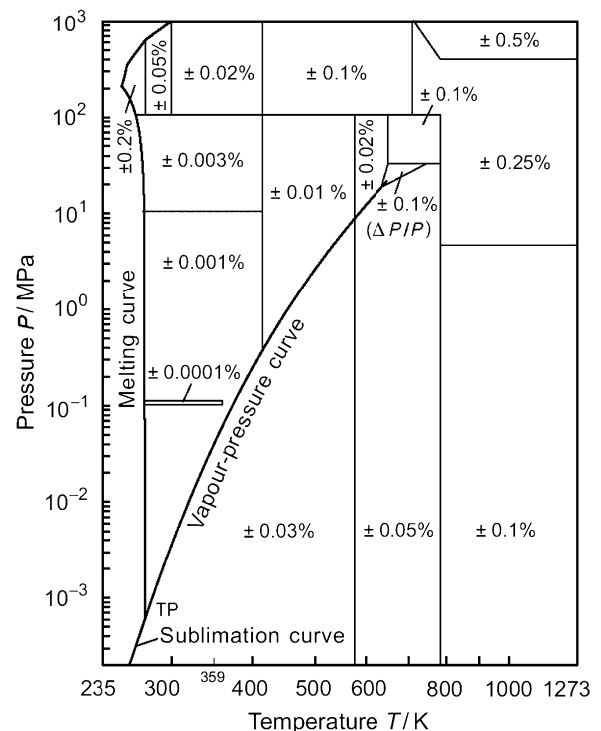


Fig. 1. Phase diagram and uncertainties in density, $u_c(\rho)/\rho$, from the IAPWS-95 formulation (IAPWS, 1996), modified (credit to Prof. W. Wagner, Bochum).

The mathematical structure of the saline Gibbs function is described in Section 5. The variables S_A , t and p are represented by dimensionless variables, x , y and z which vary between 0 and 1 in the oceanographic standard range (sometimes referred to as the “Neptunian” range of properties), making the actual function independent of the choice of measuring units and keeping the coefficients, in particular those of higher powers, within numerically reasonable orders of magnitude. For the ease of differentiation and integration, the function itself is a polynomial except for an indispensable logarithmic term resulting from Planck’s theory of ideal solutions, and the use of the square root of salinity adopted from the statistical theory of electrolytes. A brief review of existing measurements and theoretical treatments of thermodynamic properties of concentrated seawater is given in Section 6, which describes the adjustment of the new saline Gibbs energy of seawater to selected experimental data at normal pressure. In Section 7, uncertainty estimates are derived for several quantities available from the new formulation. In Appendix A, tables of basic relations, fundamental constants, computed coefficients and numerical check values are provided.

In two companion papers (McDougall et al., 2008; Feistel et al., 2008a), tabulated values of various properties, simplified, tailored formulas and algorithms as well as examples for the oceanographic application of the Gibbs function formalism will be provided, consistent with this paper and developed by WG127 for

use in sea-going, archiving and modelling activities in marine research. They will be accompanied by a digital supplement containing a comprehensive source code library for the properties of liquid water, vapour, ice and seawater, implementing the corresponding international standard formulations (IAPWS, 1996, 2006, 2008).

Combined standard uncertainties u_c are reported in this paper in brackets (ISO, 1993b), as e.g. in Table 15, from which expanded uncertainties $U = ku_c$ can be obtained by multiplying with the coverage factor $k = 2$, corresponding to a 95% level of confidence. The recommended notation of expanded uncertainties is behind a \pm sign. The short notion ‘uncertainty’ used in the following refers to combined standard uncertainties or to relative combined standard uncertainties.

2. Scales and units

In this paper, the preferred units for all quantities are their basic SI units, m, s, kg, Pa, K, J, etc. Rather than their common multiples, or even obsolete units, they very much simplify the handling of the Gibbs function and its derivatives. Given that the specific volume v is obtained from the pressure derivative of the Gibbs energy, $v = (\partial g / \partial P)_{S,T}$, at constant temperature, T , and absolute salinity, S_A , the corresponding conversion between the units, $1 \text{ m}^3 \text{ kg}^{-1} = (1 \text{ J kg}^{-1}) / (1 \text{ Pa})$, is straightforward without any numerical scaling factor. Exceptions from this rule are the absolute salinity in g kg^{-1} rather than in kg kg^{-1} , and atomic weights in g mol^{-1} rather than in kg mol^{-1} , for familiarity with their values. This has to be borne in mind when, e.g. the mass fraction of water in seawater is computed from $1 - S_A = 1000 \text{ g kg}^{-1} - S_A$.

Here and later, the subscript A at S_A is suppressed for simplicity if S_A itself is a subscript of a thermodynamic derivative.

The symbol P will be used for the absolute pressure, and p for the sea pressure (also called gauge pressure or applied pressure), relative to the pressure P_0 of one standard atmosphere, $P_0 = 101\,325 \text{ Pa}$, briefly normal pressure:

$$P = 101\,325 \text{ Pa} + p \quad (2.1)$$

In the experimental works referred to later, other pressure units used are related to Pa by ISO (1993a)

$$1 \text{ atm} = 101\,325 \text{ Pa} \quad (2.2)$$

$$1 \text{ bar} = 10 \text{ dbar} = 100\,000 \text{ Pa} \quad (2.3)$$

$$1 \text{ mmHg} = 133.3224 \text{ Pa} \quad (2.4)$$

The best measure available for the absolute salinity of standard seawater, i.e. the mass fraction of dissolved substance, is the reference-composition salinity, S_R , as defined recently by Millero et al. (2008), in short reference salinity. Traditionally, experimental seawater data have been reported in terms of the Practical Salinity (PSS-78,

Unesco, 1981, 1986), S , the chlorinity, Cl , the absolute salinity, S_A , or the Knudsen salinity, S_K .

For convenience, we formally introduce the unit conversion factors, u_{PS} and u_{Cl} , defined by

$$u_{PS} = (35.16504 \text{ g kg}^{-1}) / 35 \approx S_R / S \quad (2.5)$$

and

$$u_{Cl} = 1.80655 \times u_{PS} \quad (2.6)$$

These constants are useful to convert from practical salinity (2.5) or chlorinity (2.6) to reference salinity at various instances in this paper, and allow one to write the different salinity measures in a uniform way. For example, the reference salinity of the standard ocean, defined by the Practical Salinity $S = 35$ (Millero et al., 2008), can be written in the equivalent forms,

$$\begin{aligned} S_R &= 35.16504 \text{ g kg}^{-1} = 3.516504\% = 35 \times u_{PS} \\ &= 19.373945 \times u_{Cl} \end{aligned} \quad (2.7)$$

Thus, a Practical Salinity of $S = 35$ is equivalently described by the equation $S_R = S \times u_{PS} = 35 u_{PS}$, and a chlorinity of $Cl = 19.373945 \text{ g kg}^{-1}$ is approximately equivalent to $S_R = 19.373945 u_{Cl}$. In this way the different salinity scales can conveniently be expressed in terms of a single measure, the reference salinity, S_R . In mathematical expressions, the constants u_{PS} and u_{Cl} can formally be treated like units of salinity. The reference salinity of the standard ocean, S_{SO} , Table 16, given in Eq. (2.7), is equal to the reference salinity of KCl-normalized seawater as defined in the Reference-Composition Salinity Scale (Millero et al., 2008), briefly referred to as normal salinity.

In accord with the intention of the Reference-Composition Salinity Scale, absolute salinity, S_A , will be used as the independent salinity variable of the Gibbs function developed in this paper, sometimes simply called ‘salinity’ in the following text, which for standard seawater is approximated most accurately by the reference salinity, S_R :

$$S_A = S_R \quad (2.8)$$

We will use the symbol S_K for the ‘Knudsen salinity’ expressed in parts per thousand, “‰”. The Knudsen salinity is computed from chlorinity, “Cl‰”, that is determined by silver titration, using Knudsen’s (1901) historical equation, $S_{\text{‰}} = 0.03 + 1.805 \times Cl_{\text{‰}}$. Knudsen salinity is the mass fraction of dry substance in non-standard (Baltic) seawater remaining after evaporation as performed experimentally by S.P.L. Sørensen in 1900 (Forch et al., 1902; Lyman, 1969; Millero et al., 2008). It is not consistent with Eq. (2.7) for standard or reference seawater if the salinity is different from that of the standard ocean, the normal salinity $S_R = 35.16504 \text{ g kg}^{-1} = 35 u_{PS}$. Rather, it is given by

$$S_K = 0.03 \text{ g kg}^{-1} + 0.994453 \times S_R \quad (2.9)$$

The fundamental thermodynamic quantity temperature T was measured in the past on different practical scales used for the calibration of thermometers, IPTS-48, IPTS-68, ITS-90, and some others (Goldberg and Weir, 1992). Readings reported on these scales are commonly expressed by the symbols T_{48} , T_{68} and T_{90} . The conversion

functions between the measured values, $T_{90}(T_{68})$, etc., are nonlinear and are taken here from the algorithms given by Rusby (1991), thus being consistent with the conversion used for the pure-water formulations IAPWS-95 and IAPWS-06.

The thermodynamic temperature, T , is assumed to be equivalent to the latest scale, ITS-90, i.e.

$$T = T_{90} \quad (2.10)$$

In addition to the absolute temperature, T , the symbol t will describe values in the Celsius temperature scale, in $^{\circ}\text{C}$, relative to $T_0 = 273.15 \text{ K}$ (Preston-Thomas, 1990),

$$T/\text{K} = 273.15 + t/^{\circ}\text{C} \quad (2.11)$$

The reference point $T_0 = 273.15 \text{ K}$ for the Celsius scales is the same in IPTS-48 and IPTS-68.

Some experimental reports refer to the “ice point”, i.e. the freezing temperature of pure water at normal pressure. From the measurements of Ginnings and Corruccini (1947) and the triple-point properties of water (Guildner et al., 1976; Preston-Thomas, 1990) this freezing temperature follows to be $T = 273.152519(2) \text{ K}$ or $t = 0.002519^{\circ}\text{C}$, rather than 0°C (Feistel and Wagner, 2005, 2006; IAPWS, 2006). While these values refer to air-free water, the freezing point of air-saturated water is lowered by 2.4 mK (Doherty and Kester, 1974) to about 0.0001°C . Similarly, the boiling point of pure water at normal pressure is at $T = 373.1243 \text{ K}$ or $t = 99.9743^{\circ}\text{C}$, rather than at 100°C (Wagner and Pruß, 2002). Air solubility decreases rapidly at higher temperatures (Wagner and Pruß, 1993; IAPWS, 2004). At the boiling point, water is deaerated. More details about the ice point and the triple point are discussed in Sections 6.1 and 6.3.

Further units and conversion formulas used in Section 6 are described therein.

3. Thermodynamic potential functions

The seawater formulation proposed in this paper requires the mathematical combination of two different thermodynamic potentials, the saline Gibbs function and the Helmholtz function of pure water. In order to carry out the partial derivatives for the various thermodynamic properties, the appropriate thermodynamic rules must be considered. The required basic relations are summarized in this section.

All thermodynamic properties of a given substance at equilibrium can be derived from a single mathematical function, called the thermodynamic potential, if expressed in terms of its natural independent variables. There are many different such potential functions possible, related to each other by so-called Legendre transforms (Alberty, 2001). Although these functions are mathematically and physically equivalent, practically or numerically some of them have certain advantages or are more conveniently used. For seawater (Fofonoff, 1962; Feistel, 1993) and ice (Feistel and Hagen, 1995; Tillner-Roth, 1998; Feistel and Wagner, 2006), Gibbs functions are used because their independent variables, temperature and pressure, can be measured directly, in contrast to, e.g., entropy or density required as the input variables for other potentials. For the

description of a fluid including its two-phase region, however, a Gibbs function is numerically inconvenient because its partial derivatives (density, entropy) are two-valued on the phase transition boundary (Fig. 1) of the temperature–pressure diagram. In a temperature–density diagram, on the contrary, the two phases are coexisting over an extended region rather than just along a curve, and can be properly described by a smooth, single-valued Helmholtz function outside this region (Wagner and Pruß, 2002), even permitting a reasonable continuation into the metastable (subcooled, superheated) regimes.

Another useful thermodynamic potential function for seawater is the enthalpy depending on salinity, pressure and entropy because it provides convenient expressions for adiabatic quantities frequently used in oceanography, such as potential temperature or potential density (Feistel and Hagen, 1995). This function is briefly considered at the end of this section.

The fundamental thermodynamic relation for seawater can be written as

$$du = -Pdv + Tds + \mu dS_A \quad (3.1)$$

which states that the specific internal energy, u , of seawater can be changed by compression work, Pdv , by exchange of heat, Tds , and by exchange of salt and water, μdS_A . Here, s is the specific entropy, and $\mu = \mu^S - \mu^W$, Eq. (1.3), is the relative chemical potential (Fofonoff, 1962; §57 in Landau and Lifschitz, 1974).

The energy balance (3.1) is strictly correct only for reversible transitions between equilibrium states. Non-equilibrium processes are characterized by an irreversible production of entropy and require further considerations (Glansdorff and Prigogine, 1971; Falkenhagen et al., 1971; Ebeling and Feistel, 1982; De Groot and Mazur, 1984; Feistel and Ebeling, 1989).

For a parcel in local equilibrium, Eq. (3.1) is an exact differential, and P , T and μ can be computed by partial derivatives from the given potential function $u(S_A, s, v)$, and in turn, quantities like heat capacity or compressibility can be obtained from derivatives of these quantities using the well-known thermodynamic relations.

The specific Gibbs energy, g , is defined by the Legendre transform of u ,

$$g = u + Pv - Ts. \quad (3.2)$$

From (3.2) and (3.1), the total differential dg follows as

$$dg = v dP - s dT + \mu dS_A. \quad (3.3)$$

The natural variables of g , temperature, pressure and salinity of seawater can be measured directly by in-situ probes. Therefore, the Gibbs function is the preferred thermodynamic potential in oceanography (Fofonoff, 1962). Since (3.3) is an exact differential for a parcel in local equilibrium, the specific entropy, s , and the relative chemical potential, μ , can be obtained from partial derivatives of the given function $g(S_A, T, P)$. A list of relations between basic thermodynamic properties and the Gibbs function is given in Tables 18 and 19.

In contrast, the IAPWS-95 formulation for fluid (i.e. liquid and gaseous) water (IAPWS, 1996; Wagner and Pruß, 2002) is given in terms of the Helmholtz function,

f (i.e. the specific Helmholtz energy expressed in terms of its natural variables, temperature and specific volume, or density) defined by the Legendre transform

$$f = u - Ts = g - Pv \tag{3.4}$$

From (3.1) and (3.4), the exact differential df follows as

$$df = -P dv - s dT = \frac{P}{\rho^2} d\rho - s dT \tag{3.5}$$

For practical reasons, specific volume, v , is substituted by density, $\rho = 1/v$, as the independent variable. Consequently, $f(T, \rho)$ is expressed in this formulation in its natural independent variables T and ρ . It follows from Eq. (3.5) that the pressure is computed as $P = \rho^2(\partial f/\partial \rho)_T$, and the specific entropy as $s = -(\partial f/\partial T)_\rho$. The first and second derivatives of f are summarized in Table 1. Inverse relations, i.e. physical properties expressed in terms of derivatives of f , are given in Table 20.

The Jacobi method developed by Shaw (1935) is the mathematically most elegant way of transforming the various partial derivatives of different potential functions into each other, exploiting the convenient formal calculus of functional determinants (Margenau and Murphy, 1943; Landau and Lifschitz, 1966).

Since the IAPWS-95 formulation uses absolute temperature T and absolute pressure P as the standard variables, we will write f in these terms while the function g will be expressed here in the variables t and p , convenient for oceanographers. However, this rule is ambiguous, since e.g. the specific entropy s is the temperature derivative of both f or g , its notation is difficult to be made in the form of rigorously either $s(t)$ or $s(T)$.

For the properties of seawater, computed as partial derivatives of the Gibbs function (1.4),

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p) \tag{3.12}$$

the derivatives of g^W can be expressed in terms of the Helmholtz function f . Given t and p , the initial step is computing density from Eq. (3.7), $P = \rho^2(\partial f/\partial \rho)_T$, e.g. by Newton iteration or directly from a suitable ‘backward’ equation (Wagner and Kretschmar, 2008). From T and ρ , the other partial derivatives of g^W are available as given in Table 2. Evidently, all salinity derivatives of g^W vanish. For simplicity, we have dropped here the superscript W of f , indicating liquid water. This should not cause problems

Table 1

The partial derivatives of the Helmholtz function, $f(T, \rho)$, expressed in terms of thermodynamic coefficients

Derivative of $f(T, \rho)$	Property	Unit	Eq.
f	$u - Ts = g - P/\rho$	J kg^{-1}	(3.6)
f_ρ	P/ρ^2	$\text{J m}^3 \text{kg}^{-2}$	(3.7)
f_T	$-s$	$\text{J kg}^{-1} \text{K}^{-1}$	(3.8)
$f_{\rho\rho}$	$\frac{1}{\rho^3} (\frac{1}{\kappa_T} - 2P)$	$\text{J m}^6 \text{kg}^{-3}$	(3.9)
$f_{\rho T}$	$\alpha/(\rho^2 \kappa_T)$	$\text{J m}^3 \text{kg}^{-2} \text{K}^{-1}$	(3.10)
f_{TT}	$-c_v/T$	$\text{J kg}^{-1} \text{K}^{-2}$	(3.11)

κ_T : isothermal compressibility, α : thermal expansion coefficient, c_v : specific isochoric heat capacity (isochoric derivatives, taken at constant specific volume, are equivalent to isopycnal derivatives, i.e. at constant density).

Table 2

Partial derivatives of the Gibbs function of water, g^W , expressed as partial derivatives of the Helmholtz function, f

Derivative of $g^W(t, p)$	Equivalent in $f(T, \rho)$	Unit	Eq.
p	$\rho^2 f_\rho - P_0$	Pa	(3.13)
g_p^W	$f + \rho f_\rho$	J kg^{-1}	(3.14)
g_ρ^W	ρ^{-1}	$\text{m}^3 \text{kg}^{-1}$	(3.15)
g_t^W	f_T	$\text{J kg}^{-1} \text{K}^{-1}$	(3.16)
g_{pp}^W	$-\frac{1}{\rho^3(2f_\rho + \rho f_{\rho\rho})}$	$\text{m}^3 \text{kg}^{-1} \text{Pa}^{-1}$	(3.17)
g_{pt}^W	$\frac{f_{\rho T}}{\rho(2f_\rho + \rho f_{\rho\rho})}$	$\text{m}^3 \text{kg}^{-1} \text{K}^{-1}$	(3.18)
g_{tt}^W	$f_{TT} - \frac{\rho f_{T\rho}^2}{(2f_\rho + \rho f_{\rho\rho})}$	$\text{J kg}^{-1} \text{K}^{-2}$	(3.19)

Subscripts indicate partial derivatives with respect to the respective variables. Here, ρ is the density of liquid pure water at given T and P .

here since no Helmholtz function of seawater will be considered in this paper. It is important to note that the density ρ used as the input variable to the Helmholtz function is always the density of pure water ρ^W at given T and P rather than the density of seawater.

In Eq. (3.12), the unique separation of one function into a sum of two is subject to the additional constraint that the saline Gibbs function, $g^S(0, t, p) = 0$, vanishes for pure water. While this condition holds analogously for all derivatives of g^S with respect to t or p , this is not necessarily true for the salinity derivatives. For instance, for physical reasons, the relative chemical potential, $\mu = (\partial g^S/\partial S_A)_{t, p} = (\partial g/\partial S_A)_{t, p}$, possesses a singularity in the zero-salinity limit. This reflects mathematically the empirical fact that the complete removal of salt from seawater is practically not possible with finite effort.

To illustrate the use of Table 2, the following two examples are given.

A thermodynamic property which is a linear expression in g , e.g. the isobaric heat capacity, Table 18, is computed straight from the sum of the water and saline heat capacities, as

$$c_p = -Tg_{tt} = -Tg_{tt}^W - Tg_{tt}^S \\ = -T \left(f_{TT} - \frac{\rho f_{T\rho}^2}{(2f_\rho + \rho f_{\rho\rho})} \right) - Tg_{tt}^S = c_p^W + c_p^S. \tag{3.20}$$

Here, the saline heat capacity, c_p^S , depends only on the saline Gibbs function, g^S . The formula for the heat capacity of water, c_p^W , is determined by $-Tg_{tt}^W$ in Table 2.

On the contrary, a nonlinear expression in g , e.g. the sound speed, c , of seawater, Table 18,

$$c = g_p \sqrt{\frac{g_{tt}}{g_{tp}^2 - g_{tt}g_{pp}}} = (g_p^W + g_p^S) \\ \times \sqrt{\frac{g_{tt}^W + g_{tt}^S}{(g_{tp}^W + g_{tp}^S)^2 - (g_{tt}^W + g_{tt}^S)(g_{pp}^W + g_{pp}^S)}} \tag{3.21}$$

is related to the sound speed of pure water,

$$c^W = g_p^W \sqrt{\frac{g_{tt}^W}{(g_{tp}^W)^2 - g_{tt}^W g_{pp}^W}} \\ = \sqrt{(\rho^W)^2 \frac{f_{TT} f_{\rho\rho} - f_{T\rho}^2}{f_{TT}} + 2\rho^W f_{\rho\rho}} \tag{3.22}$$

in a complicated way, and the saline part of the sound speed, $c^S = c - c^W$, i.e. the difference between (3.21) and (3.22), is no longer a functional of solely the saline Gibbs function, g^S . To actually compute c by means of (3.21), the partial derivatives of g^W in (3.21) must be substituted by their f equivalents from Table 2 where again, we emphasize that the density argument of the Helmholtz function is the density of freshwater at the given temperature and pressure, rather than the in-situ density of seawater.

For the computation of the potential temperature, θ , the pure-water density, ρ^W , belonging to the in-situ conditions, t, p , is determined first from Eq. (3.7) by solving the equation

$$(\rho^W)^2 f_\rho(T_0 + t, \rho^W) = P_0 + p \quad (3.23)$$

Its analogue for the reference level at pressure p_r and potential temperature θ , reads

$$(\rho_\theta^W)^2 f_\rho(T_0 + \theta, \rho_\theta^W) = P_0 + p_r \quad (3.24)$$

depending on two unknowns, ρ_θ^W and θ . At both levels, the parcel is assumed to possess the same entropy, $s(S_A, t, p) = s(S_A, \theta, p_r)$. With Eq. (3.16), this condition gives

$$\begin{aligned} f_T(T_0 + t, \rho^W) + g_t^S(S_A, t, p) \\ = f_T(T_0 + \theta, \rho_\theta^W) + g_t^S(S_A, \theta, p_r) \end{aligned} \quad (3.25)$$

Combined with (3.23), this equation provides ρ_θ^W and θ .

For the computation of the potential density, ρ_θ , we find from (3.12) and (3.15) the result

$$\frac{1}{\rho_\theta} = \frac{1}{\rho_\theta^W} + g_p^S(S_A, \theta, p_r) \quad (3.26)$$

Potential enthalpy can be computed from the equations $h_\theta = h(S_A, \theta, p_r)$ and $h = g + Ts$, as

$$\begin{aligned} h_\theta = f(T_0 + \theta, \rho_\theta^W) + \rho_\theta^W f_\rho(T_0 + \theta, \rho_\theta^W) \\ + g^S(S_A, \theta, p_r) - (T_0 + \theta) f_T(T_0 + \theta, \rho_\theta^W) \\ + g_t^S(S_A, \theta, p_r) \end{aligned} \quad (3.27)$$

Formally more elegant and convenient results that are mathematically equivalent to Eqs. (3.23)–(3.27) can be obtained using the specific enthalpy, h ,

$$h(S_A, s, p) = g + Ts = u + Pv \quad (3.28)$$

$$dh = v dp + T ds + \mu dS_A \quad (3.29)$$

as an alternative thermodynamic potential function for seawater (Feistel and Hagen, 1995), complementing the Gibbs and the Helmholtz function approaches, Eqs. (3.2) and (3.4). Because of Eq. (3.29), the natural independent variables of enthalpy are pressure, entropy and salinity.

Many oceanographic processes like pressure excursions of a seawater parcel conserve salinity and entropy in very good approximation. In particular, if a parcel is moved this way to some reference pressure $p = p_r$, all its thermodynamic properties given in Table 3 can be computed at that reference level from the partial derivatives of $h(S_A, s, p_r)$. Such properties derived from the potential function h at the reference pressure are commonly referred to as ‘potential’ properties in

Table 3

Partial derivatives of the enthalpy potential function, h , expressed as partial derivatives of the Gibbs function, g

Derivative of $h(S_A, s, p)$	Equivalent in $g(S_A, t, p)$	Property	Unit	Eq.
s	$-g_t$	s	$\text{J kg}^{-1} \text{K}^{-1}$	(3.35)
h	$g - Tg_t$	h	J kg^{-1}	(3.36)
h_s	g_s	μ	J kg^{-1}	(3.37)
h_s	T	T	K	(3.38)
h_p	g_p	v	$\text{m}^3 \text{kg}^{-1}$	(3.39)
h_{ss}	$\frac{g_{ss}g_{tt} - g_{st}^2}{g_{tt}}$	$-a$	J kg^{-1}	(3.40)
h_{ss}	$-\frac{g_{st}}{g_{tt}}$	$-a$	K	(3.41)
h_{sp}	$\frac{g_{sp}g_{tt} - g_{st}g_{tp}}{g_{tt}}$	$-a$	$\text{m}^3 \text{kg}^{-1}$	(3.42)
h_{ss}	$-\frac{1}{g_{tt}}$	T/c_p	$\text{Kg K}^2 \text{J}^{-1}$	(3.43)
h_{sp}	$-\frac{g_{tp}}{g_{tt}}$	Γ	K Pa^{-1}	(3.44)
h_{pp}	$\frac{g_{tt}g_{pp} - g_{tp}^2}{g_{tt}}$	$-v\kappa_s = -\frac{v^2}{c^2}$	$\text{m}^3 \text{kg}^{-1} \text{Pa}^{-1}$	(3.45)

Subscripts indicate partial derivatives with respect to the respective variables. Γ : adiabatic lapse rate, κ_s : isentropic compressibility.

^a The quantity g_{st} appearing here is related to the thermodiffusion coefficient (§58 in Landau and Lifschitz, 1974) but has no common name or symbol.

oceanography, e.g., as

$$\begin{aligned} \text{the potential enthalpy, } h_\theta, \\ h_\theta = h(S_A, s, p) \quad \text{at } p = p_r \end{aligned} \quad (3.30)$$

the potential temperature, θ , in $^\circ\text{C}$,

$$T_0 + \theta = \left(\frac{\partial h(S_A, s, p)}{\partial s} \right)_{s,p=p_r} \quad (3.31)$$

or the potential density, ρ_θ ,

$$\rho_\theta^{-1} = \left(\frac{\partial h(S_A, s, p)}{\partial p} \right)_{s,s} \quad \text{at } p = p_r \quad (3.32)$$

Evidently, for any fixed reference pressure, p_r , the value of $h(S_A, s, p_r)$ and of all its partial derivatives remain constant during isentropic ($s = \text{const}$) and isohaline ($S_A = \text{const}$) processes.

To practically compute the potential properties (3.30)–(3.32) from the Gibbs function $g(S_A, t, p)$ of seawater, the independent variable t appearing in the expression for the enthalpy, Eq. (3.28),

$$h = g - T \left(\frac{\partial g}{\partial t} \right)_{s,p} \quad (3.33)$$

needs to be substituted by entropy, s , from numerically solving the equation

$$s = - \left(\frac{\partial g}{\partial t} \right)_{s,p} \quad (3.34)$$

for temperature as a function of salinity, entropy and pressure, $t = t(S_A, s, p)$.

In analogy to Table 2, the partial derivatives of $h(S_A, s, p)$ are obtained from those of $g(S_A, t, p)$ as shown in Table 3, to be used in the numerical implementation (Feistel et al., 2008a).

The formulas given in this section describe the way the ‘primary formulation’, i.e. the combination of the IAPWS-95 Helmholtz function with the saline Gibbs function of

this paper can properly be evaluated mathematically and numerically. These relations are designed in such a way that fully consistent results for all thermodynamic properties can be obtained with full accuracy, regardless of computation effort or speed. In two companion papers (McDougall et al., 2008; Feistel et al., 2008a), WG127 will provide simplified approximate expressions for the most important oceanographic quantities which will be regarded as “secondary standards”, using simplified and faster algorithms. These formulas may possess reduced consistency, accuracy, or range of validity compared to the primary standard they are derived from.

For temperatures below 40 °C, with only tiny deviations, the pure-water ($S = 0$) properties can also be computed using the Gibbs function (F03) determined in Feistel (2003) at zero salinity, which was derived as a convenient alternative to the IAPWS-95 formula for the Neptunian range of properties. It was determined by fitting the functions given in Table 2 to the full IAPWS-95 formula and additionally to the IAPWS-95 sound speed, in order to take advantage of the particular error sensitivity of the latter quantity. The F03 source code is available from the digital supplement of Feistel (2005). Further, the source code available from the digital supplement of Feistel et al. (2008b) implements the Release of IAPWS (1996) for pure water and vapour, and of IAPWS (2006) for ice.

4. Phase transitions of water and seawater

The validity range of the IAPWS-95 formulation for fluid water includes the vapour–liquid phase boundary, referred to as the saturation curve or vapour pressure curve, given by $T_{\text{boil}}(P)$, the boiling temperature of pure water as a function of pressure (Fig. 1). In the T – P diagram, this curve begins at the triple point ($T_t = 273.16$ K, $P_t = 611.657(10)$ Pa), where liquid, vapour and ice Ih are in mutual equilibrium, passes through the normal pressure boiling point at $T_{\text{boil}} = 373.1243$ K and 101 325 Pa, and ends at the critical point ($T_c = 647.096$ K, $P_c = 22.064$ MPa), beyond which the two fluid phases, liquid and gas, can no longer be distinguished from each other.

Along this vapour pressure curve, water vapour is in thermodynamic equilibrium with liquid water, and the chemical potentials of both phases coincide. Since the chemical potential of pure water equals its specific Gibbs energy, Eq. (1.3), the latter is a continuous function with respect to the liquid–vapour crossover. The first derivatives of the Gibbs function, however, are discontinuous on the phase transition curve, due to the different specific volumes, $v = (\partial g / \partial p)_t$, and entropies, $s = -(\partial g / \partial t)_p$, of the two phases. Thus, the Gibbs function $g(t, p)$ possesses a ‘kink’ along the vapour pressure curve $T_{\text{boil}}(p)$, which is emerging out of the smooth surface at the critical point. If additionally the metastable states of subcooled vapour and superheated liquid are considered, the Gibbs function is even multi-valued in the vicinity of the phase transition line, with the different branches of the manifold intersecting each other. This kind of qualitative geometric transition is called a cusp catastrophe in mathematics

(Poston and Stewart, 1978). An attempt at the numerical implementation of $g(t, p)$ with such properties appears difficult and inappropriate in terms of smooth and single-valued functions like polynomials.

Alternatively, in the Helmholtz rather than the Gibbs function description, the two-phase region no longer occupies a one-dimensional curve, but extends over a finite area in the T – ρ space, suitably described by a smooth and single-valued function $f(T, \rho)$, as given in the IAPWS-95 formulation. Hence, even though all thermodynamic potentials are equivalent mathematically, their applicabilities for particular purposes may vary significantly, and their suitable choice is subject to practical needs and computational convenience. Seawater with supercritical properties has recently been observed at hydrothermal vents on the sea floor (Reed, 2006); for its description the current Gibbs formulation may possibly become inconvenient in the future.

Along the melting line in Fig. 1, the chemical potential surfaces of water, $\mu^w = g^w(t, p)$, and of ice Ih, $\mu^{\text{Ih}} = g^{\text{Ih}}(t, p)$, intersect. At any given point (t, p) on either side of the curve, the particular phase with lower Gibbs energy is the stable phase, the other one is metastable.

When sea salt is dissolved in water, the freezing point is lowered by up to 8 °C at 110 g kg⁻¹, depending on the salt concentration (Feistel and Marion, 2007). Seawater is still a stable liquid phase at temperatures slightly below the freezing point of pure water. For the numerical computation of its properties from a combination of a pure-water function and a saline correction, the first one must provide reasonable values in the interval between the freezing points of water and of seawater. As described by Wagner and Pruß (2002), this is in fact the case, even though this interval is outside of the actual validity range of the IAPWS-95 formulation. In the metastable region, virtually all experimental data available are well represented by IAPWS-95, and the mathematical behaviour of the functions is reasonable and smooth. This was the result obtained by a task group appointed by IAPWS for this purpose (IAPWS, 2007; Feistel et al., 2008c). The equations for the freezing point are discussed in Section 6.3.

The situation is similar when the vapour pressure or the evaporation enthalpy of seawater needs to be computed from the related equilibrium conditions, Eqs. (6.25) and (6.34). Due to the dissolved salt, the vapour pressure of seawater at 25 °C is up to about 200 Pa lower than that of pure water (Feistel and Marion, 2007). At 80 °C, the boiling point is elevated by up to 2 °C at 120 g kg⁻¹ (Fabuss and Korosi, 1966; Bromley et al., 1974). The phase diagram of seawater is shown in Fig. 8, the equations for the boiling point are discussed in Section 6.4.

With increasing salinity, the T – P locus of the critical point of seawater can be assumed to be displaced significantly relative to that of pure water even though such measurements are not available yet. For example, the critical point of NaCl solution is well known (IAPWS, 2000). At a concentration of 120 g kg⁻¹, the critical point is located at ($T_c = 663.629$ K, $P_c = 25.686$ MPa), in contrast to the critical point ($T_c = 647.096$ K, $P_c = 22.064$ MPa) of pure water. In the ocean, critical conditions may thus be

anticipated at temperatures about 390 °C at 2600 m depth. A recent review on near-critical properties was given by Anisimov et al. (2004).

While the equilibrium between seawater and water vapour is properly described by the set of equations proposed in this paper, the real ocean interacts with humid air rather than pure vapour. The ocean water is under the pressure of the atmosphere, not just the partial pressure of vapour. The properties of maritime aerosol depend on the poorly known surface tension of concentrated brine droplets. Only in lowest-order approximation, air and water vapour in the atmosphere behave like uncorrelated ideal gases. So-called virial coefficients are used to describe their first mutual interaction terms (Harvey and Huang, 2007). The so far most accurate thermodynamic description of humid air properties is available from Hyland and Wexler (1983) and Picard et al. (2008). A more detailed discussion of this issue is beyond the scope of this paper.

5. Saline Gibbs function of seawater

The dissolution of salt in water changes its thermodynamic properties. The Gibbs function of seawater, $g(S_A, t, p)$, with salinity S_A can be written as a sum of the Gibbs function of liquid pure water, g^W , available from the IAPWS-95 formulation, $g^W(t, p) = f(T, \rho) + P/\rho$, Eq. (3.4), and a salinity correction, the saline Gibbs function of seawater, $g^S(S_A, t, p)$, as

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p), \quad (5.1)$$

with the property $g^S(0, t, p) = 0$.

At a given salinity S_A , the specific Gibbs energy of seawater, $g(S_A, t_0, p_0)$, at the reference point $t_0 = 0^\circ\text{C}$ in temperature and $p_0 = 0\text{Pa}$ in sea pressure can be extended into the surrounding t - p space by an integral over the total differential, Eq. (3.3), along an arbitrary path between (t_0, p_0) and (t, p) , as e.g.,

$$g(S_A, t, p) = g(S_A, t_0, p_0) + \int_{t_0}^t dt' \left[\frac{\partial g(S_A, t', p_0)}{\partial t'} \right]_{S, p_0} + \int_{p_0}^p dp' \left[\frac{\partial g(S_A, t, p')}{\partial p'} \right]_{S, t} \quad (5.2)$$

Subtracting off the corresponding equation for $g^W(t, p)$ and using thermodynamic rules and partial integration, this integral can be rearranged for the specific saline Gibbs energy, $g^S(S_A, t, p)$, of seawater relative to pure water, Eq. (5.1), in the form

$$g^S(S_A, t, p) = g_0^S(S_A) - t s_0^S(S_A) + \int_0^t dt' (t' - t) \frac{c_{p,0}^S(S_A, t')}{T_0 + t'} + \int_0^p dp' v^S(S_A, t, p') \quad (5.3)$$

The different terms appearing in expression (5.3) are the saline specific volume, $v^S(S_A, t, p)$, as a function of three variables, salinity, temperature and pressure, the saline specific heat capacity, $c_{p,0}^S(S_A, t) \equiv c_p^S(S_A, t, 0)$, as a function of two variables, absolute salinity and temperature at normal pressure, as well as the saline specific Gibbs

energy, $g_0^S(S_A) \equiv g^S(S_A, 0, 0)$, and the saline specific entropy, $s_0^S(S_A) \equiv s^S(S_A, 0, 0)$, both as functions of merely one variable, absolute salinity S_A , at normal pressure and 0°C .

To easily carry out analytical integration and differentiation, the saline Gibbs potential (5.3) is expressed mathematically as a polynomial-like function (Feistel, 1993, 2003; Feistel and Hagen, 1995),

$$g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ g_{1jk} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j z^k \quad (5.4)$$

of the dimensionless variables, x , y , z , representing the salinity, S_A , by

$$S_A = S_u \times x^2 \quad (5.5)$$

the ITS-90 Celsius temperature, t , by

$$T - T_0 = t = t_u \times y \quad (5.6)$$

and the sea pressure, p , by

$$P - P_0 = p = p_u \times z \quad (5.7)$$

The unit-dependent scaling constants g_u , S_u , t_u and p_u are given in Table 16. The logarithmic term in (5.4) is consistent with Planck's theory of ideal solutions (Falkenhagen et al., 1971). The quadratic scaling (5.5) results from the theory of electrolytes, in which the Debye radius, Eq. (6.8), of the ion-ion pair correlation function is inversely proportional to the root of the ion concentration, caused by the ionic long-range Coulomb interaction.

Corresponding to the pure-water part, $g^W(t, p)$, of Eq. (5.1), the terms proportional to x^0 have been omitted from Eq. (5.4). The mathematical structure of (5.4) permits a one-to-one association of certain groups of its coefficients to the physically distinct terms of (5.3) by comparing equal powers in pressure and temperature, as

$$\int_0^p dp' v^S(S_A, t, p') = g_u \times \sum_{k>0} \sum_j \sum_{i>1} g_{ijk} x^i y^j z^k \quad (5.8)$$

$$\int_0^t dt' (t' - t) \frac{c_{p,0}^S(S_A, t')}{T_0 + t'} = g_u \times \sum_{j>1} \sum_{i>1} g_{ij0} x^i y^j \quad (5.9)$$

$$s_0^S(S_A) = -\frac{g_u}{t_u} \times \left\{ g_{110} x^2 \ln x + \sum_{i>1} g_{i10} x^i \right\} \quad (5.10)$$

$$g_0^S(S_A) = g_u \times \left\{ g_{100} x^2 \ln x + \sum_{i>1} g_{i00} x^i \right\} \quad (5.11)$$

These functions will subsequently be discussed in the following sections. The specific volume, $v^S(S_A, t, p)$, i.e. the pressure-dependent term (5.8), will be adopted from the 2003 Gibbs function (Feistel, 2003) in the form of the related unaltered set of coefficients, g_{ijk} . The other three functions (5.9)–(5.11) will be determined by fitting their coefficients to experimental data of heat capacities, freezing points, vapour pressures, mixing heats and theoretical limiting laws, respectively, in the range -6 to 95°C and 0 – 120g kg^{-1} at $p = 0$, and making use of the thermodynamic reference point conditions, Eqs. (6.13) and (6.14).

6. Determination of the saline Gibbs energy

There are only few experimental works published on standard seawater at temperatures or salinities beyond those of ‘Neptunian’ waters. In particular, there are no such works known to the author at high pressure, no measurements of compressibility or sound speed, thermal expansion, haline contraction, conductivity, or any properties at very low temperature, e.g. for sea ice. A selection of publications outside the oceanographic standard range is given in Table 4, including theoretical studies and observations of artificial or non-standard seawaters.

For the future development of a more accurate high-pressure Gibbs function at elevated temperatures and salinities, comprehensive measurements of densities and their derivatives with respect to S_A , t and p for standard seawater will be indispensable. The same is true for the low-temperatures range down to the freezing point at high salinities or high pressures.

In this paper, six works out of this selection were considered as appropriate and sufficiently accurate for the regression carried out to determine the Gibbs energy at -6 to 80 °C, 0 – 120 g kg $^{-1}$ and normal pressure. In addition to those, further sets used here are derived from theoretical considerations (e.g. the limiting laws) or regard thermal and colligative properties in the oceanographic standard range 0 – 40 °C, 0 – 40 g kg $^{-1}$ that had been exploited already for the determination of F03. For each measured sample X_i^{exp} at the temperature t_i , salinity S_i and $p = 0$, the associated mathematical expression, $X_i^{\text{calc}}(S, t|\mathbf{x})$, is derived from the Gibbs and Helmholtz functions,

depending on the set of adjustable coefficients, g_{ijk} , subsummed here as the vector of unknowns, \mathbf{x} . With the weights, ω_i , estimated from the experimental uncertainties, the total least-square sum

$$\Omega^2(\mathbf{x}) = \sum_i \Omega_i^2 = \sum_i \frac{[X_i^{\text{calc}}(S_i, t_i|\mathbf{x}) - X_i^{\text{exp}}]^2}{\omega_i^2}, \quad (6.1)$$

carried out over the entire data set, was minimized with respect to the coefficients, \mathbf{x} . The system of regression equations implied

$$\frac{\partial}{\partial \mathbf{x}} \Omega^2 = 0 \quad (6.2)$$

was solved numerically for \mathbf{x} , simultaneously for all of the 602 data points, Table 7, and all of the 21 adjustable parameters. This way the coefficients of the saline Gibbs function, Eqs. (5.9)–(5.11), at normal pressure, salinity up to 120 g kg $^{-1}$ and temperature up to 80 °C were determined from the experimental and model data, as reported in Table 17 of the Appendix A. Details of this procedure, in particular the definition of the functions Ω_i for each group of data, are described successively in the following sections. In Section 6.4, measurements are used at pressures slightly different from $p = 0$.

6.1. Limiting laws and reference states

With respect to powers of salinity, S_A , the theoretical series expansion of the saline Gibbs energy has the form (Landau and Lifschitz, 1966; Falkenhagen et al., 1971;

Table 4

Selection of experiments and theoretical studies on equilibrium properties of natural and artificial seawaters outside the standard oceanographic range

Article	S_A (g kg $^{-1}$)	T (°C)	P (MPa)	Comment
This paper, Table 5	35	−5 to 95	0.1	A, S
Sun et al. (2008)	0–40	0–374	0.1–100	A, S
Feistel and Marion (2007), Table 6	0–110	−6 to 25	0.1–100	A, S
Millero and Pierrot (2005)	0–120	0–200	0.1	S, X
Anati (1999)	0–280	20–35	0.1	D
Lvov and Wood (1990)	0–500	0–700	0.1–1000	NaCl
Krumgalz and Millero (1982a, b)	0–300	0–50	0.1	D, A, X
Chen (1982)	0–60	0–40	0.1–100	NaCl
Liphard et al. (1977)	0–60	20	100–200	NaCl, X
Bromley et al. (1974)	2–71	60–120	0.1	P, X
Bromley (1973)	0–300	25	0.1	A
Singh and Bromley (1973)	0–120	0–75	0.1	P, X
Robinson and Wood (1972)	25–300	25	0.1	A
Liu et al. (1971)	50–350	75–300	0.1–9	A, X
Daley et al. (1970)	10–280	0–200	0.1	S, X
Grunberg (1970)	0–160	0–180	0.1–1	A, S, X
Connors (1970)	10–60	0–30	0.1	X
Bromley et al. (1970a, b)	0–120	0–200	0.1–1.5	P, X
Bromley (1968)	0–120	25	0.1	P, X
Bromley et al. (1967)	10–120	2–80	0.1	P, X
Stoughton and Lietzke (1967)	20–280	25–260	0.1	A
Bromley et al. (1966)	11–117	2–80	0.1	A, P, X
Fabuss and Korosi (1966)	34–103	20–180	0.1	A, S
Rush and Johnson (1966)	30–350	25	0.1	A, X
Higashi et al. (1931)	10–160	0–175	0.1–0.5	X

Bold—data used in this paper, S—work regarding standard or Atlantic seawater, D—Dead Sea water, P—Pacific seawater, A—artificial seawater, NaCl—sodium chloride solution, X—experimental work (rather than theoretical model).

Feistel, 2003),

$$g(S_A, t, p) = N_S k T S_A \ln \frac{S_A}{S_{SO}} + (c_{20} + c_{21} T) S_A + g^{LL}(S_A, T, P) + O(S_A^2) \quad (6.3)$$

The logarithmic term, resulting from the theory of ideal solutions, is independent of pressure and linear in temperature. Comparing equal powers with Eq. (5.4), we infer the following relations for the coefficients:

$$g_{100} \times g_u = 2N_S S_u k T_0 \quad (6.4)$$

$$g_{110} \times g_u = 2N_S S_u k t_u \quad (6.5)$$

$$g_{ijk} = 0 \quad \text{for } j > 1 \text{ or } k > 0 \quad (6.6)$$

The coefficients g_{100} and g_{110} computed from Eqs. (6.4) and (6.5) are listed in Table 17. They are only slightly different from those given in Feistel (2003).

Derived from the statistical theory of dilute electrolytes (Landau and Lifschitz, 1966; Falkenhagen et al., 1971; Feistel 2003), the limiting law term, g^{LL} , is $O(S_A^{3/2})$,

$$g^{LL}(S_A, T, P) = -\frac{k T v^W(T, P)}{12\pi} [\kappa_D(S_A, T, P)]^3. \quad (6.7)$$

Here, k is Boltzmann's constant, N_S is the number of particles per mass of dissolved sea salt with reference composition (Millero et al., 2008), and $S_{SO} = 35u_{PS}$, Eq. (2.5), is the salinity of the standard ocean, Table 16, being equal to that of KCl-normalized standard seawater, in brief normal salinity. The Debye parameter, κ_D , i.e. the reciprocal Debye radius of the ion cloud, $r_D = 1/\kappa_D$, of seawater is given by

$$\kappa_D(S_A, T, P) = Ze \sqrt{\frac{N_S S_A}{\epsilon_0 \epsilon^W(T, P) v^W(T, P) k T}} \quad (6.8)$$

Here, $\epsilon^W(T, P)$ is the static dielectric constant of water (IAPWS, 1997; Wagner and Kretzschmar, 2008), and $v^W(T, P)$ the specific volume of water (IAPWS-95).

The constants c_{20} and c_{21} in (6.3) depend on the definition of the seawater reference state and will be discussed below. Further constants and variables in Eqs. (6.3) and (6.8) are given in Table 13–16.

The reference composition in Table 15 was determined experimentally at 25 °C and normal salinity (Millero et al., 2008), $S_{SO} = 35u_{PS}$. It enters into the limiting-law coefficients via two composition-dependent values, namely the valence number Z^2 and the particle number $N_S = N_A/M_S$ (or equivalently, the molar mass M_S) at 0 °C and at infinite dilution. The ionic stoichiometry of the dissolved sea salt components is controlled by chemical solute–solute and solvent–solute reactions, depending on temperature, pressure and salinity. Thus, this difference in S_A and t will cause an uncertainty of the limiting law coefficients which is unknown but assumed to be small.

The terms of the potential function, Eq. (5.4), corresponding to Eq. (6.7) read at normal pressure

$$g_3(S_A, t, 0) = g_u \sum_j g_{3j0} x^3 y^j \quad (6.9)$$

The coefficients g_{3j0} of this expression are significant mainly for very dilute solutions. Their determination is

Table 5

Values of the Debye radius, $r_D = 1/\kappa_D$, Eq. (6.8), and of the limiting law of the Gibbs energy, g^{LL} , Eq. (6.7), at normal pressure and normal salinity, $S_R = 35u_{PS}$

t (°C)	r_D (nm)	g^{LL} (J kg ⁻¹)
-5	0.369968	-1940.69
0	0.369036	-1990.75
5	0.368140	-2041.77
10	0.367263	-2093.95
15	0.366393	-2147.43
20	0.365522	-2202.32
25	0.364646	-2258.69
30	0.363762	-2316.61
35	0.362867	-2376.14
40	0.361961	-2437.33
45	0.361042	-2500.25
50	0.360110	-2564.95
55	0.359166	-2631.47
60	0.358209	-2699.88
65	0.357239	-2770.22
70	0.356258	-2842.55
75	0.355266	-2916.92
80	0.354263	-2993.39
85	0.353250	-3072.01
90	0.352227	-3152.86
95	0.351196	-3235.98

more accurate from the theoretical formula (6.7) than from experimental seawater data. In principle, the coefficients can be directly computed from the Taylor expansion of (6.7) with respect to Celsius temperature. However, the values of formula (6.7) are computed from experimental data as well; their uncertainties result mainly from the dielectric function, $\epsilon^W(T, P)$, which has an estimated absolute uncertainty of 0.04 in the range of interest here (IAPWS, 1997).

We have computed 21 values from Eq. (6.7), given in Table 5, to minimize the expression:

$$\Omega_{LL}^2 = \frac{1}{\omega_{LL}^2} \sum \{g_3(S_A, t, 0) - g^{LL}\}^2 \quad (6.10)$$

with a required r.m.s. of $\omega_{LL} = 1 \text{ J kg}^{-1}$. The resulting scatter was 0.09 J kg^{-1} , Fig. 2.

The arbitrary coefficients g_{200} and g_{210}

$$g_{200} \times g_u = c_{20} S_u + c_{21} T_0 S_u + N_S S_u k T_0 \ln \frac{S_u}{S_{SO}} \quad (6.11)$$

$$g_{210} \times g_u = c_{21} t_u S_u + N_S S_u k t_u \ln \frac{S_u}{S_{SO}} \quad (6.12)$$

are subject to the definition of the seawater reference state by specifying the two free constants, c_{20} and c_{21} . The related proposal (WG127, 2006; Feistel et al., 2008c) specifies the arbitrary constants corresponding to the saline specific entropy and the saline specific enthalpy for the standard ocean state as

$$s^S(S_{SO}, t_{SO}, p_{SO}) = s^W(T_t, P_t) - s^W(T_0, P_0) \quad (6.13)$$

$$h^S(S_{SO}, t_{SO}, p_{SO}) = u^W(T_t, P_t) - h^W(T_0, P_0) \quad (6.14)$$

Here, u^W , h^W and s^W are the specific internal energy, enthalpy and entropy of liquid water of the IAPWS-95 formulation, respectively. The definitions (6.13) and (6.14)

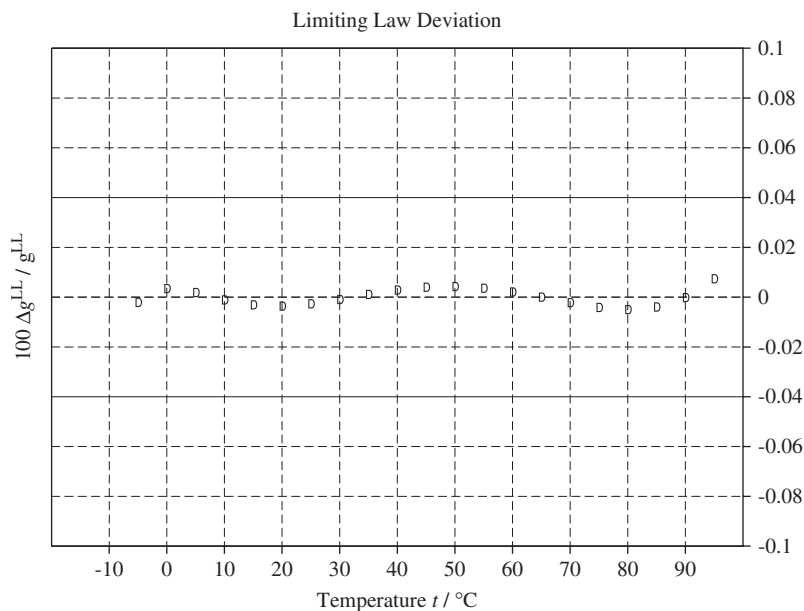


Fig. 2. Deviation of the limiting law, g^{LL} , Table 5, from the related term of the Gibbs function, g_3 , Eq. (6.9). The estimated uncertainty of the g^{LL} values is indicated as 0.04%.

imply entropy and enthalpy of seawater vanish at the standard ocean surface pressure. They provide absolute values for the relative thermodynamic functions at the seawater reference state in terms of IAPWS-95 values, so that the saline Gibbs function is independent of the choice of the IAPWS-95 reference state.

In particular, definitions (6.13) and (6.14) have the following properties (WG127, 2006):

- (i) the free constants of the saline Gibbs energy, g^S , are being specified, rather than those of the complete Gibbs energy, g , of seawater,
- (ii) the reference state definitions (6.13) and (6.14) do not impose any conditions on the IAPWS-95 formulation,
- (iii) definitions (6.13) and (6.14) do not require any explicit numerical values to be given,
- (iv) the right-hand sides of (6.13) and (6.14) are independent of the choice of the two free constants within IAPWS-95, and so are the saline quantities $s^S(S_{\text{SO}}, t_{\text{SO}}, p_{\text{SO}})$ and $h^S(S_{\text{SO}}, t_{\text{SO}}, p_{\text{SO}})$. In other words, the IAPWS reference state definition does not impose any conditions onto the intended WG127 formulation, $g^S(S, t, p)$,
- (v) the definitions are different from the ones given in Feistel (2003) only by the tiny misfit of $g(0, t_{\text{SO}}, p_{\text{SO}})$ from Feistel (2003) to $g^{\text{W}}(T_0, P_0)$ from IAPWS-95, thus being comfortably consistent for oceanographers,
- (vi) the numerical absolute values of $s(S_{\text{SO}}, t_{\text{SO}}, p_{\text{SO}})$ and $h(S_{\text{SO}}, t_{\text{SO}}, p_{\text{SO}})$ for seawater do depend on the IAPWS-95 reference state in the same way as do $s^{\text{W}}(T_t, P_t)$ and $u^{\text{W}}(T_t, P_t)$ from IAPWS-95.

The coefficients g_{200} and g_{210} were determined from (6.13) and (6.14) after all other coefficients had been

computed from the comparison with experiments, and are given in Table 17.

In the experimental practice, two fundamental reference points are used, defined in terms of phase transitions of water, the triple point and the ice point. At the triple point, liquid water, vapour and ice are in equilibrium. At the ice point, liquid water and ice are in equilibrium at normal pressure. For clarification and unique specification of these properties, it is useful to take a closer look at some details here. More data and further relevant conclusions related to the definition and numerical implementation of reference state conditions are provided by Feistel et al. (2008c), also including seawater properties.

The common *physical triple point* of water is the thermodynamic equilibrium state between liquid water, vapour and ice. The actual standard definition of pure water is Vienna Standard Mean Ocean Water (VSMOW), consisting of several isotopes of hydrogen and oxygen as found under ambient conditions (IAPWS, 2005). The isotopic composition specified in 2005 for the SI-definition of the triple point is similar (BIPM, 2006). If the particular liquid, gaseous and solid phases possess mutually different isotope ratios, equilibrium temperatures can vary over an interval of estimated $40 \mu\text{K}$ width, rather than being fixed to just a single, unique “point”. Different isotope fractionations between liquid, gas and ice correspond to different equilibrium temperatures between those phases (Nicholas et al., 1996; White et al., 2003; Chialvo and Horita, 2003; Feistel and Wagner, 2006; Polyakov et al., 2007). Consequently, the uncertainty of any ITS-90-calibrated thermometer cannot be smaller than $40 \mu\text{K}$ even if its precision in resolving temperature differences may be in the order of $1 \mu\text{K}$ or less (e.g. Bettin and Toth, 2006), unless the isotopic ratios of all phases are

rigorously specified in the temperature scale definition, and carefully established in the lab. In a recent review of uncertainties related to ITS-90 temperature measurements given by Rudtsch and Fischer (2008), the typical effect of isotopic composition variations on the triple point temperature is estimated to $10\ \mu\text{K}$, while the combination with other error sources leads to a combined uncertainty of $70\ \mu\text{K}$ for the calibration of Standard Platinum Resistance Thermometers.

The ITS-90 scale defines the unit kelvin by setting the temperature value at the triple point to exactly $273.16\ \text{K}$ (Preston-Thomas, 1990; BIPM, 2006).

The experimental triple point in the T - P space, i.e. the vapour pressure of water at $273.16\ \text{K}$, was determined by Guildner et al. (1976) to $P_t = 611.657(10)\ \text{Pa}$.

The numerical IAPWS-95 triple point is defined mathematically by equal chemical potentials and pressures of liquid water and vapour at exactly $273.16\ \text{K}$. Its properties computed from a quadruple-precision (128 bit) implementation of IAPWS-95, rounded to double precision (64 bit), are (Feistel et al., 2008c):

$$\begin{aligned} T &= 273.16\ \text{K} \\ P &= 611.654771007894\ \text{Pa} \\ g &= 0.611781703456383\ \text{J kg}^{-1} \\ \rho^{\text{W}} &= 999.792520031621\ \text{kg m}^{-3} \\ \rho^{\text{Vap}} &= 0.00485457572477859\ \text{kg m}^{-3} \end{aligned} \quad (6.15)$$

In this implementation, the improved coefficients n_0^1 and n_0^2 of the IAPWS-95 formulation adjusted to the reference point conditions of vanishing entropy and internal energy of the liquid phase at this triple point take the values, rounded to double precision

$$\begin{aligned} n_0^1 &= -8.32044648374969 \\ n_0^2 &= 6.68321052759323 \end{aligned} \quad (6.16)$$

The numerical IAPWS-95/06 triple point can be defined mathematically by equal chemical potentials of liquid water, vapour and ice Ih. Its properties computed from a quadruple-precision implementation of IAPWS-95 and IAPWS-06, rounded to double precision, are (D.G. Wright, priv. comm.):

$$\begin{aligned} T &= 273.160000093071\ \text{K} \\ P &= 611.654775144545\ \text{Pa} \\ g &= 0.611781707593825\ \text{J kg}^{-1} \end{aligned} \quad (6.17)$$

These high-precision implementations show that a small modification of the adjustable coefficient $g_{00} = -0.632020233449497 \times 10^6\ \text{J kg}^{-1}$ published with the Gibbs function of ice (Feistel and Wagner, 2006; IAPWS, 2006), to the more accurate value $g_{00} = -0.632020233335886 \times 10^6\ \text{J kg}^{-1}$ is required to correct the numerical IAPWS-95/06 triple-point temperature from the value (6.17) to $T = 273.160000000000\ \text{K}$ in all 15 digits. The most accurate triple-point properties of liquid water, vapour and ice computed from suitably adjusted IAPWS Releases are reported in Feistel et al. (2008c).

Practically, all triple point definitions discussed before are consistent with each other within their experimental

uncertainties and natural physical fluctuations. Numerically, however, the related values are slightly different. In this paper, the numerical IAPWS-95 triple point data (6.15) were used as the definite reference point.

The ice point, i.e. the melting temperature, $T = 273.152519(2)\ \text{K}$, of ice at normal pressure, $P = 101\ 325\ \text{Pa}$, is equal to the freezing temperature of air-free liquid water. Its very small uncertainty of $2\ \mu\text{K}$ is estimated from the assumption that the triple-point temperature of $273.16\ \text{K}$ is exact by definition (Feistel and Wagner, 2005, 2006). The freezing temperature of air-saturated water is about $T = 273.1501\ \text{K}$. The temperature of an ice-water mixture used to fix the ice point in a lab may vary between both temperatures depending on the amount of gases dissolved in water, i.e. within about $2\ \text{mK}$ uncertainty. See Section 6.3 for more details.

6.2. Heat capacity

The specific isobaric heat capacity of seawater, c_p , is computed from the Gibbs function, g , as

$$c_p(S_A, t, p) = -(T_0 + t) \left(\frac{\partial^2 g}{\partial t^2} \right)_{S_A, p} \quad (6.18)$$

The measurements of heat capacity published by Bromley et al. (1970a) were carried out in a pressurized bomb under the vapour pressure of the solution, depending on temperature and salinity. These data were not used for the fit because of the uncertainties of the pressure correction function (5.8) at high salinities and temperatures.

The heat capacity data c_p^{B67} reported by Bromley et al. (1967) were measured at atmospheric pressure, salinities up to $120\ \text{g kg}^{-1}$ and temperatures up to $80\ ^\circ\text{C}$. The salinities of Pacific and Atlantic seawater samples were determined by titration of chlorinity, Cl , and converted to salinity, S_K , from Knudsen's (1901) formula. Since the offset in this formula originates from Baltic Sea water and is invalid for samples from the Atlantic or Pacific, we have converted Bromley's salinity values back to reference salinity by means of Eq. (2.9). The calories reported were converted to absolute joules by $1\ \text{cal} = 4.184\ \text{J}$. The temperatures are assumed to be given on the IPTS-48 scale.

The correction of the heat capacity values regarding the temperature scale is, as recommended by Goldberg and Weir (1992),

$$\delta c_p = (T_{48} - T_{90}) \frac{dc_p}{dT} + c_p \frac{d(T_{48} - T_{90})}{dT} \quad (6.19)$$

While the first term is negligible here, the second one gives a maximum correction at $0\ ^\circ\text{C}$ of 0.07% or $3\ \text{J kg}^{-1}\ \text{K}^{-1}$ and is of the order of the experimental uncertainty, which was estimated by the authors as $u_c(c_p^{B67}) = 4\ \text{J kg}^{-1}\ \text{K}$, used below to set the required accuracy of the fit.

Pure water measurements were not reported by Bromley et al. (1967). To compute the differences between

seawater and water, we have used the correlation equation reported in their paper

$$\frac{c_p^{B67}(t_{48})}{\text{cal g}^{-1} \text{K}^{-1}} = 1.0049 - 3.2506 \times 10^{-4} \left(\frac{t_{48}}{^{\circ}\text{C}}\right) + 3.8013 \times 10^{-6} \left(\frac{t_{48}}{^{\circ}\text{C}}\right)^2 \quad (6.20)$$

By means of this formula, the 221 measured values c_p^{B67} of Bromley et al. (1967) were additively corrected for their pure-water part before minimizing the expression

$$\Omega_{B67}^2 = \frac{1}{\omega_{B67}^2} \sum \left\{ T \left(\frac{\partial^2 g^S}{\partial t^2} \right)_{S_A, P_0} + c_p^W(T, P_0) + [c_p^{B67} - c_p^{B67}(t_{48})] \frac{dT_{48}}{dT_{90}} \right\}^2 \quad (6.21)$$

with a required r.m.s. deviation of $\omega_{B67} = 4 \text{ J kg}^{-1} \text{ K}^{-1}$, using c_p^W from IAPWS-95. The resulting scatter was $3.5 \text{ J kg}^{-1} \text{ K}^{-1}$ and is shown in Fig. 3.

Millero et al. (1973a) published electrical power ratios $r(S, t) = \Delta W/W$ of their Picker calorimeter with an overall uncertainty of 0.5% to compute heat capacities $c_p(S, t, 0)$ of seawater at atmospheric pressure from the formula,

$$\frac{c_p(S, t, 0)}{c_p(0, t, 0)} = (1 + r(S, t)) \frac{\rho(0, t, 0)}{\rho(S, t, 0)} \quad (6.22)$$

using densities $\rho(S, t, 0)$ of seawater and pure-water densities $\rho(0, t, 0)$ and heat capacities $c_p(0, t, 0)$. Here, the Practical Salinity S must be converted to absolute salinity by Eq. (2.5), $S_A = S \times u_{ps}$. We have minimized the

corresponding sum over the 48 reported points, $r(S, t_{68})$, as

$$\Omega_{MPD73}^2 = \frac{1}{\omega_{MPD73}^2} \sum \left\{ T \left(\frac{\partial g^S}{\partial t} \right)_{S_A, P_0} + c_p^W(T, P_0) \times \left[(1 + r(S, t_{68})) \left(\frac{v^S(S, t, 0)}{v^W(T, P_0)} + 1 \right) - 1 \right] \right\}^2 \quad (6.23)$$

with a required r.m.s. deviation of $\omega_{MPD73} = 0.5 \text{ J kg}^{-1} \text{ K}^{-1}$, using the saline specific volume $v^S = (\partial g^S / \partial p)_{S_A, t}$ and the water properties c_p^W and v^W from IAPWS-95. The result of the fit is shown in Fig. 3, with an r.m.s. of $0.57 \text{ J kg}^{-1} \text{ K}^{-1}$.

Millero and Pierrot (2005) reported unpublished measurements of Millero, Oglesby and Duer from 1980 for the heat capacity of seawater at 10, 20, 30 and 40 °C (assumed IPTS-68) with an estimated uncertainty of $\omega_{MP05} = 0.5 \text{ J kg}^{-1} \text{ K}^{-1}$ (F.J. Millero, priv. comm.). We have minimized the sum over 41 data points,

$$\Omega_{MP05}^2 = \frac{1}{\omega_{MP05}^2} \sum \left\{ T \left(\frac{\partial^2 g^S}{\partial t^2} \right)_{S_A, P_0} + c_p^W(T, P_0) + [c_p^{MP05} - c_p^{MPD73}(t_{68})] \frac{dT_{68}}{dT_{90}} \right\}^2 \quad (6.24)$$

using the pure-water properties c_p^W from IAPWS-95 and c_p^{MPD73} from Millero et al. (1973a). The resulting scatter with an r.m.s. of $1.3 \text{ J kg}^{-1} \text{ K}^{-1}$ is shown in Fig. 3.

6.3. Freezing point

The freezing temperature $t_f(S_A, p)$ of seawater with salinity S_A at the pressure p obeys the condition of

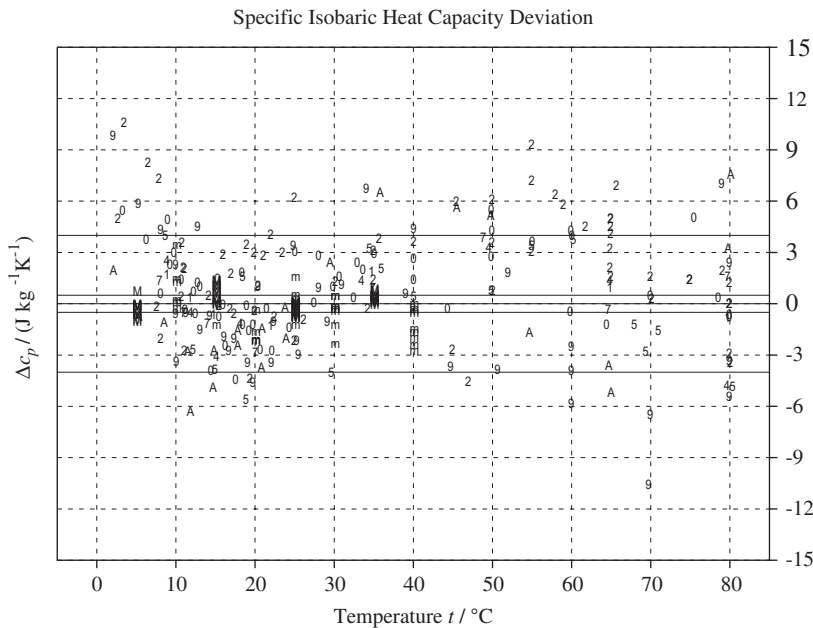


Fig. 3. Deviation of heat capacity measurements from the computed values, Eq. (6.18). M: Millero et al. (1973b) with r.m.s. $0.57 \text{ J kg}^{-1} \text{ K}^{-1}$, m: Millero and Pierrot (2005) with r.m.s. $1.3 \text{ J kg}^{-1} \text{ K}^{-1}$, 0-A: Bromley et al. (1967) with r.m.s. $3.5 \text{ J kg}^{-1} \text{ K}^{-1}$. Here, symbols indicate 10 g kg^{-1} salinity intervals, from 0 for $S_A = 0-10 \text{ g kg}^{-1}$ to A for $S_A = 100-110 \text{ g kg}^{-1}$. The experimental uncertainties are shown by horizontal lines.

thermodynamic equilibrium between seawater and the naturally abundant hexagonal ice phase I (ice Ih) that the chemical potentials of water must be the same in both phases,

$$\mu^W(S_A, t_f, p) = \mu^{lh}(t_f, p) \quad (6.25)$$

The chemical potential of water in seawater, μ^W , is (Feistel and Hagen, 1995, 1998)

$$\begin{aligned} \mu^W = g - S_A \times \left(\frac{\partial g}{\partial S_A} \right)_{t,p} = g^W(t, p) \\ + g^S(S_A, t, p) - S_A \times \left(\frac{\partial g^S}{\partial S_A} \right)_{t,p} \end{aligned} \quad (6.26)$$

The chemical potential of ice equals its specific Gibbs energy, g^{lh} ,

$$\mu^{lh}(t, p) \equiv g^{lh}(t, p) \quad (6.27)$$

The Gibbs function of ice is available from IAPWS (2006), its details are described by Feistel and Wagner (2005, 2006). Hence, Eq. (6.25) for the freezing point reads

$$g^{lh}(t_f, p) - g^W(t_f, p) = g^S(S_A, t_f, p) - S_A \times \left(\frac{\partial g^S}{\partial S_A} \right)_{t_f, p} \quad (6.28)$$

The freezing temperature resulting from Eq. (6.28) at $S_A = 0$ and normal pressure is $t_f^{\text{pure}}(0) = 0.002519^\circ\text{C}$ (Feistel and Wagner, 2006). Its freezing point depression due to saturation with air is 2.4 mK, but slightly less for seawater, 1.9 mK (Doherty and Kester, 1974). The corresponding correction to the freezing point of air-free water can be estimated as $t_f^{\text{air}}(S_A) = t_f^{\text{pure}}(S_A) - (2.4 - S_A/(70 \text{ g kg}^{-1}))\text{mK}$. The readings of Doherty and Kester (1974),

t_f^{DK74} , describe the freezing point lowering of air-saturated water due to salt, $t_f^{\text{air}}(S_A) = t_f^{\text{air}}(0) + t_f^{\text{DK74}}$. Combining these relations and converting from IPTS-68 to ITS-90 by the function t_{90_68} , the freezing points are obtained from

$$t_f^{\text{pure}}(S_A) = 2.519 \text{ mK} + t_{90_68} \left(t_f^{\text{DK74}} - \frac{S_A}{70} \frac{\text{mK}}{\text{g kg}^{-1}} \right) \quad (6.29)$$

for air-free water conditions assumed in this paper, with an estimated uncertainty of 2 mK.

In order to satisfy the equilibrium condition (6.28), we have minimized the sum

$$\begin{aligned} \Omega_{\text{DK74}}^2 = \frac{1}{\omega_{\text{DK74}}^2} \sum \left[g^S(S_A, t, 0) - S_A \times \left(\frac{\partial g^S}{\partial S_A} \right)_{t,p=0} \right. \\ \left. - g^{lh}(t, 0) + g^W(t, 0) \right]^2 \end{aligned} \quad (6.30)$$

over the measured 32 points (S, t) with $t = t_f^{\text{pure}}(S_A)$ from Eq. (6.29). The required r.m.s. of the fit is $\omega_{\text{DK74}} = 3 \text{ J kg}^{-1}$, the resulting r.m.s. is 2.0 J kg^{-1} , corresponding to 1.6 mK in the freezing temperatures. The scatter of the fit is shown in Fig. 4.

At salinities higher than 40 g kg^{-1} , the function $g_0^S(S_A)$, Eq. (5.3) is insufficiently determined from available experimental data. The freezing temperatures computed from the Gibbs–Pitzer model (Feistel and Marion, 2007) are derived from Pitzer equations for the particular chemical constituents of sea salt, independent of direct seawater measurements. None the less, they are in excellent agreement (2 mK) with the data of Doherty and Kester (1974). We have used 22 computed Gibbs–Pitzer freezing points, (t_f, S_A), at salinities between 5 and

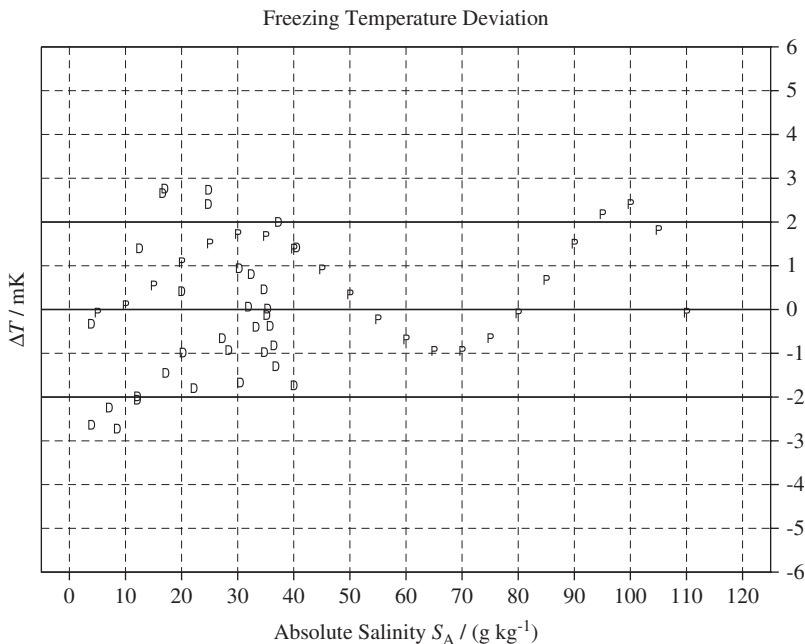


Fig. 4. Deviation of freezing temperature data from computed freezing points, Eq. (6.28). D: measurements from Doherty and Kester (1974), Eqs. (6.29) and (6.28), with an r.m.s. of 1.6 mK, P: model values from Feistel and Marion (2007), with an r.m.s. of 1.2 mK, Table 6. The experimental uncertainty of 2 mK is indicated by horizontal lines.

Table 6

Freezing temperatures, t_f , of air-free seawater computed from the Gibbs–Pitzer function of seawater (Feistel and Marion, 2007) in conjunction with the Gibbs function of ice (Feistel and Wagner, 2006)

S_A (g kg ⁻¹)	t_f (°C)
5	-0.2695
10	-0.5360
15	-0.8037
20	-1.0741
25	-1.3480
30	-1.6258
35	-1.9081
40	-2.1950
45	-2.4871
50	-2.7845
55	-3.0875
60	-3.3965
65	-3.7116
70	-4.0332
75	-4.3615
80	-4.6969
85	-5.0397
90	-5.3902
95	-5.7487
100	-6.1158
105	-6.4917
110	-6.8771

110 g kg⁻¹, given in Table 6, to minimize the sum

$$\Omega_{\text{FM07}}^2 = \frac{1}{\omega_{\text{FM07}}^2} \sum \left[g^S(S_A, t, 0) - S_A \left(\frac{\partial g^S}{\partial S_A} \right)_{t,p=0} - g^{\text{lh}}(t, 0) + g^{\text{W}}(t, 0) \right]^2 \quad (6.31)$$

The required r.m.s. of the fit is $\omega_{\text{FM07}} = 10 \text{ J kg}^{-1}$, the resulting r.m.s. is 1.5 J kg^{-1} , corresponding to 1.2 mK in the freezing temperatures. The scatter of the fit is shown in Fig. 4.

6.4. Vapour pressure

Robinson (1954) published measurements on the vapour pressure, $P^{\text{vap}}(S_A)$, of seawater with salinity S_A at 25 °C, in the form of the ratios, $r_{\text{R54}}(S_A)$,

$$r_{\text{R54}}(S_A) = \frac{P^{\text{vap}}(0) - P^{\text{vap}}(S_A)}{P^{\text{vap}}(0)} \quad (6.32)$$

for chlorinities Cl between 10 and 22 g kg⁻¹, i.e. salinities $S_A = 10 u_{\text{Cl}} \dots 22 u_{\text{Cl}}$, Eq. (2.6). At the temperature of $t_{48} = 25 \text{ °C}$ ($t = 24.985 \text{ °C}$), the vapour pressure of pure water, $P^{\text{vap}}(0) = 3167.1 \text{ Pa}$, is available from IAPWS-95.

The corresponding pressure value used by Robinson (1954), 23.756 mmHg = 3167.2 Pa, differs from the present one by only 0.003%. The temperature scale conversion is important here since the modern vapour pressure value at $t = 25 \text{ °C}$ is 3169.9 Pa, deviating by 0.09%. Hence, the common formula of Weiss and Price (1980) for the vapour pressure of seawater, derived from Robinson's (1954) measurements and claimed to be accurate as 0.015%, requires temperature scale conversion before its use.

The experimental vapour pressure values of seawater can be computed from (6.32) as

$$P^{\text{vap}}(S_A) = [1 - r_{\text{R54}}(S_A)] \times P^{\text{vap}}(0) \\ = [1 - r_{\text{R54}}(S_A)] \times 3167.1 \text{ Pa} \quad (6.33)$$

At the theoretical vapour pressure, $P \approx P^{\text{vap}}(S_A)$, the chemical potentials of vapour, $\mu^{\text{vap}} = g^{\text{vap}}$, and of water in seawater, μ^{W} , have equal values, i.e., t and p must obey

$$g^{\text{vap}}(t, p) = \mu^{\text{W}}(S_A, t, p) = g(S_A, t, p) \\ - S_A \times \left(\frac{\partial g(S_A, t, p)}{\partial S_A} \right)_{t,p} \quad (6.34)$$

After separating the water part of the Gibbs energy, g^{W} , in Eq. (6.34), we have minimized the sum

$$\Omega_{\text{R54}}^2 = \frac{1}{\omega_{\text{R54}}^2} \sum \left\{ g^S(S_A, t, p) - S_A \left(\frac{\partial g^S(S_A, t, p)}{\partial S_A} \right)_{t,p} + g^{\text{W}}(t, p) - g^{\text{vap}}(t, p) \right\}^2 \quad (6.35)$$

at 13 points $p = P^{\text{vap}}(S_A) - P_0$ computed from Eq. (6.33), and g^{W} computed from IAPWS-95. Note that P^{vap} is an absolute pressure less than P_0 . The uncertainty of the pressure measurements is estimated as 0.003 mmHg or about 0.02%, equivalent to $u_c(P^{\text{vap}})/\rho^{\text{vap}} \approx \omega_{\text{R54}} = 30 \text{ J kg}^{-1}$ in the chemical potential. The scatter of this fit has an r.m.s. of 0.002% or 0.065 Pa in vapour pressure, corresponding to 2.8 J kg^{-1} in the chemical potential, Fig. 5. Thus, the experimental uncertainty estimate appears too pessimistic.

The vapour pressure data of Grunberg (1970) were excluded from the fit because they were measured using 'natural' seawater of unspecified origin, and the salinities reported in g kg⁻¹ were determined by an unspecified method. None the less, these data are represented fairly well up to 120 g kg⁻¹ by this fit (Fig. 9).

Bromley et al. (1974) published measurements on boiling point elevation. For the temperature t given, the vapour pressure of pure water, $P = P^{\text{vap}}(0, t)$, can be computed from IAPWS-95. The 32 measured values of boiling point elevation, Δt , of seawater under the same vapour pressure, $P^{\text{vap}}(S_A, t + \Delta t) = P_0 + p$, are assumed to satisfy Eq. (6.34) and are used to minimize the condition,

$$\Omega_{\text{B74}}^2 = \frac{1}{\omega_{\text{B74}}^2} \sum \left\{ g^S(S_A, t_{\text{sw}}, p) - S_A \left[\frac{\partial g^S(S_A, t_{\text{sw}}, p)}{\partial S_A} \right]_{t,p} + g^{\text{W}}(t_{\text{sw}}, p) - g^{\text{vap}}(t_{\text{sw}}, p) \right\}^2 \quad (6.36)$$

where $t_{\text{sw}} = t + \Delta t$ is the boiling temperature of seawater. The estimated uncertainty of the boiling points is 1 mK, the required r.m.s. was $\omega_{\text{B74}} = 10 \text{ J kg}^{-1}$. The r.m.s. of the fit was 9.1 J kg^{-1} in the chemical potential, or 1.3 mK in the temperature. The data scatter is shown in Fig. 6.

6.5. Mixing heat

When two seawater samples with the masses m_1, m_2 and absolute salinities S_1, S_2 are mixed at constant temperature, a certain amount of heat, Q , will be produced. The final absolute salinity, S_A , of the sample

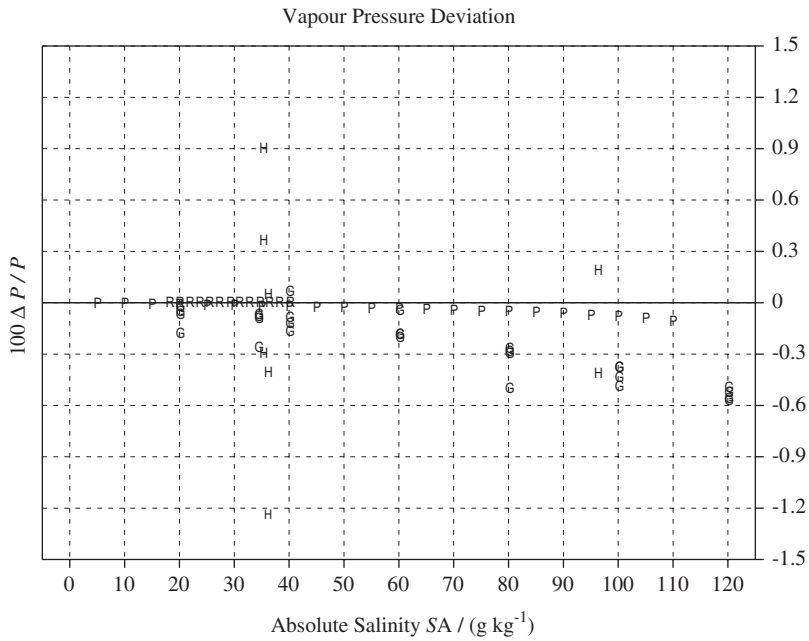


Fig. 5. Deviation of vapour pressure measurements from those computed from Eq. (6.34). R: Robinson (1954) at 25 °C with uncertainty $u_c(P)/P = 0.02\%$ and r.m.s. 0.002%, G: Grunberg (1970) at 20–80 °C with estimated uncertainty $u_c(P)/P = 0.1\%$ and r.m.s. 0.3%, H: Higashi et al (1931) at 20–80 °C with estimated uncertainty $u_c(P)/P = 0.5\%$ and r.m.s. 0.6%. P: Values computed from the Gibbs-Pitzer function of Feistel and Marion (2007) with r.m.s. 0.05%. Only Robinson's (1954) data were used for the fit.

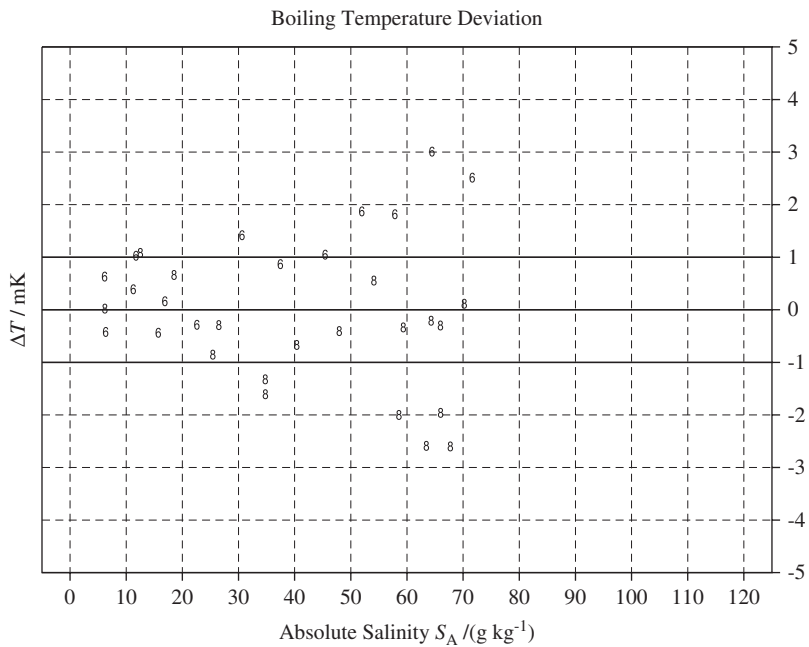


Fig. 6. Deviation of boiling point elevations measured by Bromley et al. (1974) at 60 and 80 °C, from the temperature computed from Eq. (6.34), indicated by the symbols 6 and 8, respectively. The estimated uncertainty was 1 mK, the r.m.s. of the scatter was 1.3 mK. The experimental uncertainty is shown by horizontal lines.

with the total mass, $m = m_1 + m_2$, is

$$S_A = w_1 S_1 + w_2 S_2 \tag{6.37}$$

Here, $w_1 = m_1/m$ and $w_2 = m_2/m$ are the mass fractions of the two samples. During the mixing process, a certain

mass of salt, $\Delta m = m_1 \times |S_A - S_1| = m_2 \times |S_A - S_2|$, is exchanged between the samples, and the same mass of water in the opposite direction. We refer to the quantity ΔS ,

$$\Delta S = \frac{\Delta m}{m} = w_1 w_2 |S_1 - S_2| \tag{6.38}$$

as the “mixing salinity” of this process, which is a measure of the distance from equilibrium of the initial inhomogeneous state. The mixing heat, $Q = mh_{\text{mix}}^{\text{exp}}$, is computed from the specific mixing enthalpy, h_{mix} ,

$$h_{\text{mix}}^{\text{calc}} = h^S(S_A, t, 0) - w_1 h^S(S_1, t, 0) - w_2 h^S(S_2, t, 0) \quad (6.39)$$

The sign of mixing heat is commonly defined as final minus initial enthalpy (Möbius and Dürselen, 1973; Kluge and Neugebauer, 1976).

The saline enthalpies, h^S , are computed from the saline Gibbs function, g^S , as

$$h^S = g^S - (T_0 + t) \left(\frac{\partial g^S}{\partial t} \right)_{S,p} \quad (6.40)$$

Bromley (1968) reported seawater mixing experiments at $t_{48} = 25^\circ\text{C}$ (IPTS-48 scale assumed) with an uncertainty estimate of 1 cal for Q . For the fit, 33 samples with initial masses m_1, m_2 and reference salinities S_1, S_2 up to 108 g kg^{-1} were used with their mixing heats $Q = mh_{\text{mix}}^{\text{exp}}$, converted by $4.1840 \text{ J cal}^{-1}$. We have minimized the sum,

$$\Omega_{\text{B68}}^2 = \frac{1}{\omega_{\text{B68}}^2} \sum [h^S(S_A, t, 0) - w_1 h^S(S_1, t, 0) - w_2 h^S(S_2, t, 0) - h_{\text{mix}}^{\text{exp}}]^2 \quad (6.41)$$

over these data points (m_1, S_1, m_2, S_2, Q) , with a required r.m.s. residual of $\omega_{\text{B68}} = 1 \text{ J kg}^{-1}$. The regression produced an r.m.s. deviation of 0.75 J kg^{-1} , as shown in Fig. 7.

Millero et al. (1973a) published experimental data of diluting seawater samples from Practical Salinities S_1 up to 42, to S at temperatures t (assumed IPTS-48 scale) from

0 to 30°C , reporting relative enthalpies, q ,

$$q = \frac{h^S(Su_{\text{PS}}, t, 0)}{S} - \frac{h^S(S_1 u_{\text{PS}}, t, 0)}{S_1} \quad (6.42)$$

with an uncertainty of 5 cal eq^{-1} . We have minimized the sum

$$\Omega_{\text{MHH73}}^2 = \frac{1}{\omega_{\text{MHH73}}^2} \sum [h^S(Su_{\text{PS}}, t, 0) - w_1 h^S(S_1 u_{\text{PS}}, t, 0) - h_{\text{mix}}^{\text{exp}}]^2 \quad (6.43)$$

over these 120 data points (S_1, S, t, q) , with mass fractions. The required r.m.s. was $\omega_{\text{MHH73}} = 10 \text{ J kg}^{-1}$. The resulting scatter with r.m.s. 3.3 J kg^{-1} is displayed in Fig. 7.

Connors (1970) published experimental data of mixing seawater samples with equal volumes of salinities S_1, S_2 up to 61 g kg^{-1} at temperatures t (assumed IPTS-48 scale) from 2 to 25°C , reporting the resulting temperature changes, Δt , related to the enthalpy balance

$$w_1 h^S(S_1, t, 0) + w_2 h^S(S_2, t, 0) = h^S(S_A, t + \Delta t, 0) \quad (6.44)$$

With Eq. (6.39) we thus find

$$h_{\text{mix}} = h^S(S_A, t, 0) - h^S(S_A, t + \Delta t, 0) \approx -c_p \Delta t \quad (6.45)$$

The estimated uncertainty is 5%. The mass fractions, $w_1 = \rho_1 / (\rho_1 + \rho_2)$ and $w_2 = 1 - w_1$, are computed from the densities, $\rho(S_A, t, p) = (\partial g / \partial p)_{S_A}^{-1}, t$.

We have minimized the sum with $h_{\text{mix}}^{\text{exp}} = -c_p \Delta t$,

$$\Omega_{\text{C70}}^2 = \frac{1}{\omega_{\text{C70}}^2} \sum [h^S(S_A, t, 0) - w_1 h^S(S_1, t, 0) - w_2 h^S(S_2, t, 0) - h_{\text{mix}}^{\text{exp}}]^2 \quad (6.46)$$

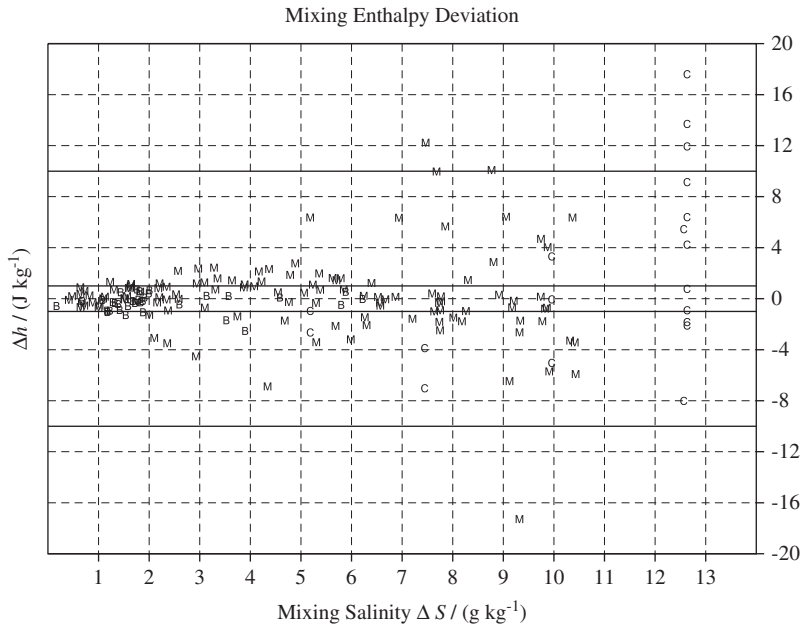


Fig. 7. Deviation $\Delta h = h_{\text{mix}}^{\text{exp}} - h_{\text{mix}}^{\text{calc}}$ of experimental mixing enthalpies from computed ones, Eq. (6.39). The mixing salinity, ΔS , is defined in Eq. (6.38). B: 33 data points from Bromley (1968) at 25°C , scattering with an r.m.s. of 0.75 J kg^{-1} . M: 120 data points from Millero et al. (1973b) from 0 to 30°C , with an r.m.s. of 3.3 J kg^{-1} . C: 19 data points from Connors (1970) from 2 to 25°C , with an r.m.s. of 7.2 J kg^{-1} . R.m.s. values required for the fit are indicated by horizontal lines.

over these 19 data points ($S_1, S_2, t, \Delta t$), with a required r.m.s. of $\omega_{C70} = 10 \text{ J kg}^{-1}$. The regression resulted in an r.m.s. deviation of 7.2 J kg^{-1} , as shown in Fig. 7.

7. Uncertainty estimates of the Gibbs function

7.1. Summary

The Gibbs function of seawater, Eq. (5.1), is valid for IAPSO Standard Seawater in certain phase space regions inside the salinity, temperature and pressure range

$$0 \leq S_A \leq 120 \text{ g kg}^{-1}, -12^\circ\text{C} \leq t \leq 80^\circ\text{C} \text{ and } -0.1 \text{ Pa} \leq p \leq 100 \text{ MPa} \tag{7.1}$$

as shown in Fig. 8.

The box-shaped volume (7.1) includes in particular the ‘Neptunian’ validity region (A) of ambient ocean water in the range

$$0 \leq S_A \leq 42 \text{ g kg}^{-1}, t_f \leq t \leq 40^\circ\text{C} \text{ and } 0 \text{ Pa} < p \leq 100 \text{ MPa} \tag{7.2}$$

The freezing temperature $t_f(S_A, p)$ is defined by Eq. (6.25).

The low-pressure region (B) of validity is restricted to the intervals

$$0 \leq S_A \leq 50 \text{ g kg}^{-1}, t_f \leq t \leq 40 \text{ K} \text{ and } p^{\text{vap}} \leq p \leq 0 \text{ Pa} \tag{7.3}$$

The vapour pressure $p^{\text{vap}}(S_A, t)$ is defined by Eq. (6.34).

The validity region (C) is the extension to concentrated seawater and to high temperature at normal pressure,

$$0 \leq S_A \leq 120 \text{ g kg}^{-1}, t_f \leq t \leq 80^\circ\text{C} \text{ and } p = 0 \text{ Pa} \tag{7.4}$$

In this two-dimensional S_A - t region, outside its intersection with the regions (A), (B) or (D), the pressure derivatives of the Gibbs function, g_p, g_{Sp}, g_{Tp} and g_{pp} in Tables 17 and 18 return only extrapolated values for the density and its derivatives outside their range of validity.

Here and in the following, the term ‘‘extrapolated’’ describes the numerical evaluation of the formula beyond its declared range of validity. In Fig. 8, the region (C) is a surface rather than a volume, having zero thickness in the p direction. In this region, outside its intersection with (A), (B), (D) or (E), quantities that rely on derivatives of the Gibbs function with respect to pressure (such as specific volume, thermal expansion coefficient, etc.) do not necessarily possess accurate values. While these quantities can formally be calculated from the Gibbs function, they are strictly outside of the range of validity for these quantities. Nevertheless, where uncertainties can be estimated for these values, they are usable if these uncertainties are properly considered.

Note that—quite generally—an uncertainty estimate of a given quantity, say density, does not imply the reliability of its derivative, say compressibility. As a simple example, the formula $y = A \sin(kx)$ approximates the equation $y(x) = 0$ well within an uncertainty of $u_c(y) = |A|/\sqrt{2}$. However, knowing an estimate for A does not permit any uncertainty estimate to be made for dy/dx .

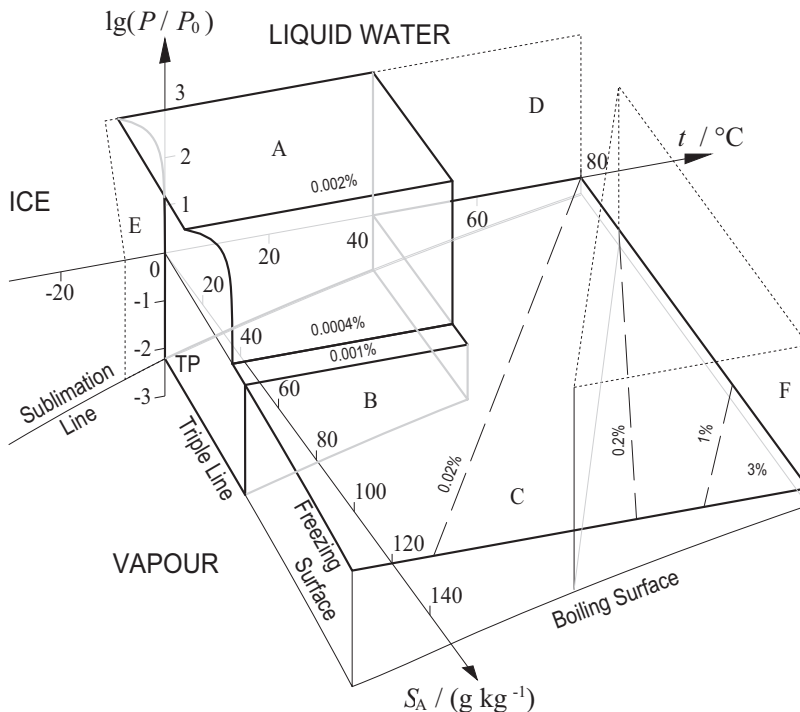


Fig. 8. Phase diagram of seawater with the regions (A–F) of the S_A - t - P space, explained in the text. The range of validity of the Gibbs function of seawater, Eq. (5.1), is shown in bold. Percentage values provide estimated uncertainties of seawater density, $u_c(\rho)/\rho$. Dashed lines indicate extrapolated ranges of extrapolated density, Table 11. ‘‘TP’’ is the common triple point (gas–liquid–solid) of pure water. The freezing surface is defined by Eq. (6.25), the boiling surface by Eq. (6.34), the triple line obeys both equations. The sublimation line is the phase equilibrium between vapour and ice.

The validity region (D) is the zero-salinity limit of dilute seawater in the range,

$$S_A = 0 \text{ g kg}^{-1}, t_f \leq t \leq 80^\circ\text{C} \text{ and } p^{\text{vap}} \leq p \leq 100 \text{ MPa} \quad (7.5)$$

which is inside the validity range of the IAPWS-95 formulation. In this two-dimensional t - p region (D), outside its intersection with the regions (A), (B) or (C), the salinity derivatives of the Gibbs function, g_S and g_{Sp} in Table 19 return only extrapolated values outside their range of validity. For physical reasons, the relative chemical potential and the chemical potential of sea salt possess logarithmic singularities for $S_A \rightarrow 0$.

The region (E) is the extrapolation range of liquid pure-water properties into the solid-phase region, between the freezing temperatures of pure water and of seawater, and into the gas-phase region, between the vapour pressures of pure water and of seawater. For the pure-water reference function, g^{W} , of Eq. (5.1), this mathematical extrapolation is required to values of t or p where seawater is a stable liquid phase but pure water is a subcooled or superheated metastable liquid phase. Due to salinity, the freezing point depression can be up to 8 K, the boiling point elevation up to 2 K (Feistel et al., 2008c).

In the prism-shaped region (F), the numerical extrapolation of the density derivatives g_{Sp} , g_{Tp} and g_{pp} in Tables 18 and 19 (which appear in particular in the expressions for compressibility or sound speed) outside their validity range results in values obviously not reasonable or even invalid. For the pressure range $p^{\text{vap}} \leq p \leq 100 \text{ MPa}$, this region is found inside a triangle given by the conditions $t/^\circ\text{C} + 0.45 S/(\text{g kg}^{-1}) > 89$, $S_A \leq 120 \text{ g kg}^{-1}$, and $t \leq 80^\circ\text{C}$. In particular, the use of these derivatives is restricted to $t < 35^\circ\text{C}$ at the highest salinity, $S_A = 120 \text{ g kg}^{-1}$, and to $S_A < 20 \text{ g kg}^{-1}$ at the highest temperature, $t = 80^\circ\text{C}$.

The range of validity of the Reference-Composition Salinity Scale is restricted by the solubility of the sea salt constituents of standard seawater. Related saturation concentrations are only incompletely known by now and are reviewed recently by Marion and Kargel (2008).

The estimated experimental uncertainties of the quantities used in this paper for the regression of the saline specific Gibbs energy at normal pressure are given in Table 7. The uncertainties regarding the adopted density from the 2003 Gibbs function are given in Table 8. Table 9 summarizes the uncertainties of the PVT properties of this formulation, see also Section 7.2 for more details about the uncertainty of density. Table 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 Gadhomi (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).

Table 9

Estimated uncertainties of PVT properties of the Gibbs function of this paper

Quantity	S_A (g kg ⁻¹)	t (°C)	p (Mpa)	Value	Unit	Reference
$u_c(\rho)/\rho$	0–40	0–40	0	4	ppm	Millero et al. (1976)
$u_c(\rho^S)/\rho$	30–40	–2 to 30	1–100	4	ppm	Bradshaw and Schleicher (1970)
$u_c(\rho)/\rho$	40–50	15–30	0	10	ppm	Poisson and Gadhoumi (1993)
$u_c(\rho)/\rho$	5–40	0–40	0–10	10	ppm	Chen and Millero (1976), IAPWS (1996)
$u_c(\rho)/\rho$	5–40	0–40	10–100	20	ppm	Chen and Millero (1976), IAPWS (1996)
$u_c(\rho)/\rho$	0–110	0–25	0–100	400	ppm	Feistel and Marion (2007)
$u_c(\rho)/\rho$	40–120	20–40	0	300	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	0–40	40–60	0	400	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	40–80	40–60	0	900	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	0–40	60–80	0	1400	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	80–120	40–60	0	3000	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	40–80	60–80	0	4000	ppm	Grunberg (1970)
$u_c(\rho)/\rho$	80–120	60–80	0	13 000	ppm	Grunberg (1970)
$u_c(\alpha)$	10–30	–6 to 1	0.7–33	0.6	ppm K ⁻¹	Caldwell (1978)
$u_c(c)/c$	29–43	0–35	0–2	30	ppm	Del Grosso (1974)
$u_c(c)/c$	29–43	0–30	0.1–5	30	ppm	Del Grosso (1974)
$u_c(c)/c$	33–37	0–5	0–100	50	ppm	Del Grosso (1974), IAPWS (1996)

Table 10Estimated uncertainties of thermal and colligative properties computed from the Gibbs function of this paper at $p = 0$

Quantity	S_A (g kg ⁻¹)	t (°C)	Value	Unit	Reference
$u_c(p^{\text{vap}})/p^{\text{vap}}$	20–120	20–80	0.1	%	Grunberg (1970)
$u_c(p^{\text{vap}})/p^{\text{vap}}$	35–95	25–76	0.5	%	Higashi et al. (1931)
$u_c(\phi)/\phi$	17–38	25	0.2	%	Robinson (1954)
$u_c(\phi)/\phi$	10–120	0–25	0.3	%	Bromley et al. (1974)
$u_c(\phi)/\phi$	4–40	0	0.2	%	Millero and Leung (1976)
$u_c(c_p^S)$	0–40	0–40	0.5	J kg ⁻¹ K ⁻¹	Millero et al. (1973a, b)
$u_c(c_p^S)$	0–40	5–35	0.5	J kg ⁻¹ K ⁻¹	Millero et al. (1973b)

summarizes the uncertainties of the thermal and colligative properties of this formulation, see also Sections 7.3 for more details about the uncertainty of the osmotic coefficient.

7.2. Density

The F03 Gibbs function (Feistel, 2003) is limited in its validity to salinities up to 42 g kg⁻¹ and temperatures up to 40 °C, where its uncertainty for the density of standard seawater at normal pressure is 0.0004%, and 0.001% up to 50 g kg⁻¹. To estimate the uncertainties outside this region, the experimental densities of Grunberg (1970) were compared with data ρ_{calc} computed from the equation

$$(\rho_{\text{calc}})^{-1} = \rho^{\text{W}}(T, P)^{-1} + \rho^{\text{F03}}(S, t, p)^{-1} - \rho^{\text{F03}}(0, t, p)^{-1} \quad (7.6)$$

For salinities up to 120 g kg⁻¹ and temperatures up to 80 °C, the deviations are reported in Table 11 and displayed in Fig. 9. The IAPWS-95 values (IAPWS, 1996), ρ^{W} , are reliable over the entire temperature range up to 80 °C, Fig. 1. By extrapolation, ρ_{calc} from Eq. (7.6) represents the artificial seawater data of Grunberg (1970) correctly within their uncertainty of 0.02% up to 100 g kg⁻¹ at 20 °C, up to 80 g kg⁻¹ at 40 °C, and still better than 0.1% up to 60 g kg⁻¹ at 60 °C.

Density of this formulation at high salinity up to 110 g kg⁻¹ and high pressure up to 100 MPa but low

Table 11Density deviation $(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{calc}}$ in % between the density data, ρ_{exp} , of artificial seawater from Grunberg (1970), and ρ_{calc} , computed from Eq. (7.6)

S_A (g kg ⁻¹)	$t = 20$ °C	$t = 40$ °C	$t = 60$ °C	$t = 80$ °C
0	0.02	-0.03	-0.03	-0.01
20	0.00	-0.03	-0.06	-0.22
35	-0.01	-0.02	-0.02	-0.15
40	-0.01	-0.01	-0.01	-0.09
60	-0.02	0.00	0.07	0.26
80	-0.01	0.01	0.20	0.82
100	0.01	0.04	0.35	1.54
120	0.05	0.07	0.55	2.44

The reported experimental uncertainty is 0.02%. The data within this limit are shown in bold. The pressure used for the computation is 101 325 Pa, except for the rightmost column with 101 325.3 Pa.

temperature up to 25 °C was compared with a Pitzer model by Feistel and Marion (2007). Since that model is derived from completely independent data sources, this comparison may serve for the uncertainty estimate of 400 ppm over the region considered.

7.3. Osmotic coefficient

The osmotic coefficient ϕ of seawater can be defined by the difference between the chemical potentials of pure water and of water in seawater. It can be computed from

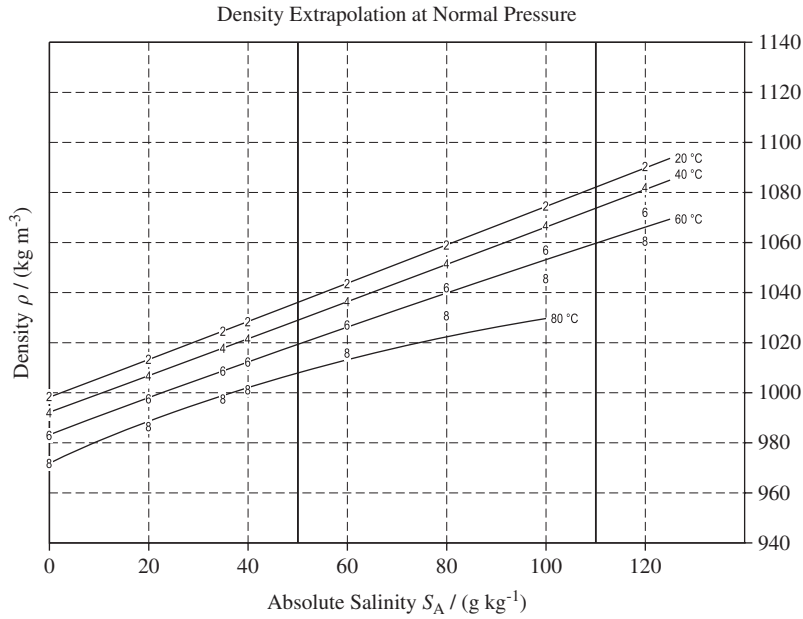


Fig. 9. Comparison of seawater densities at high salinities and temperatures. Curves: computed from Eq. (7.6) at normal pressure and IPTS-68 temperatures as indicated. Their validity range is up to 50 g kg^{-1} and $40 \text{ }^\circ\text{C}$. Symbols represent data of artificial seawater from Grunberg (1970), 2: $20 \text{ }^\circ\text{C}$, 4: $40 \text{ }^\circ\text{C}$, 6: $60 \text{ }^\circ\text{C}$, 8: $80 \text{ }^\circ\text{C}$. The vertical lines indicate the validity limit of Eq. (7.6) in salinity (50 g kg^{-1}) at temperatures up to $40 \text{ }^\circ\text{C}$, and the low-temperature saturation salinity (110 g kg^{-1}) at temperatures up to $25 \text{ }^\circ\text{C}$ of natural seawater (Feistel and Marion 2007).

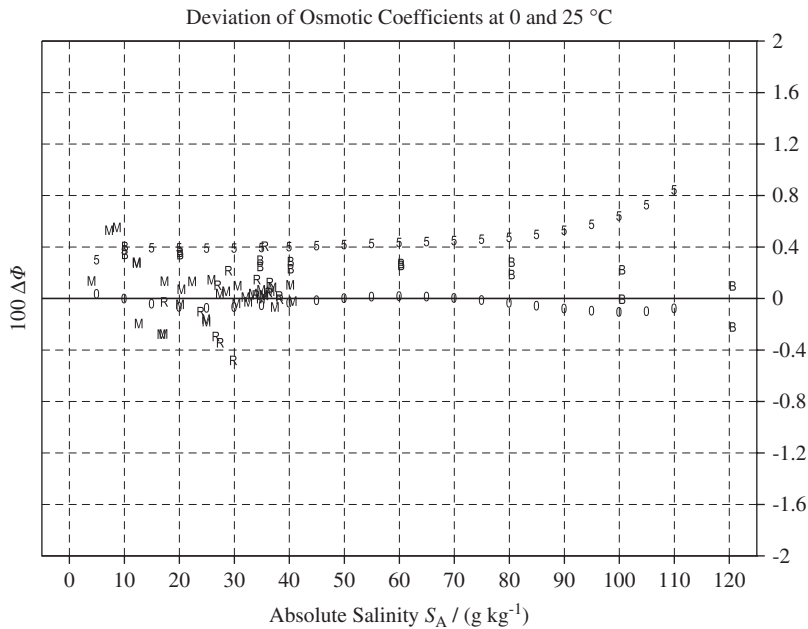


Fig. 10. Deviation of reported osmotic coefficients from those computed from Eq. (7.8), not used for the regression in this paper. R: Robinson (1954) at $25 \text{ }^\circ\text{C}$, B and b: Bromley et al. (1974) at 0 and $25 \text{ }^\circ\text{C}$, M: Millero and Leung (1976) at $0 \text{ }^\circ\text{C}$, 0 and 5: Feistel and Marion (2007) at 0 and $25 \text{ }^\circ\text{C}$.

the saline Gibbs function g^S by means of the formula (Feistel and Marion, 2007)

$$-mRT\phi = g^S - S_A \left(\frac{\partial g^S}{\partial S_A} \right)_{t,p} \quad (7.7)$$

or, rearranged, as

$$\phi = - \frac{1 - S_A}{N_S S_A kT} \left[g^S - S_A \left(\frac{\partial g^S}{\partial S_A} \right)_{t,p} \right] \quad (7.8)$$

Table 12

Scatter of reported osmotic coefficients, not used for the regression in this paper, with respect to those computed from Eq. (7.8)

Source	S_A (g kg ⁻¹)	t (°C)	Points	r.m.s.
Robinson (1954)	17–38	25	14	0.22%
Bromley et al. (1974)	10–120	0.25	16	0.27%
Millero and Leung (1976)	4–40	0	31	0.19%

Here, $m = S_A / [(1 - S_A) \times M_S]$ is the molality (moles of salt per mass of water), M_S is the mean atomic weight of sea salt, Table 13, $R = N_A \times k$ is the molar gas constant, Table 13, and $(1 - S_A)$ is the mass fraction of water in seawater. Values of the osmotic coefficient of seawater are available at 25 °C from Robinson (1954) and Bromley et al. (1974), and at 0 °C from Millero and Leung (1976) and Bromley et al. (1974).

Robinson's (1954) data were derived from vapour pressure measurements, Bromley's et al. (1974) data from boiling point elevation measurements up to salinities of 70 g kg⁻¹, and the osmotic coefficients of Millero and Leung (1976) were computed from the freezing point data of Doherty and Kester (1974). For these reasons, no regression regarding the osmotic coefficients was performed, rather, the particular original data were used for the fits in this paper. The agreement between the reported osmotic coefficients and those computed from this formulation, Fig. 10 and Table 12, is satisfactory, none the less.

8. Summary

A new general equation of state for seawater is presented in the form of a thermodynamic Gibbs potential, $g(S_A, t, p)$, composed of the sum of freshwater and saline components, Eq. (1.4). It is expressed in terms of the International Temperature Scale of 1990 and the absolute salinity of standard seawater, estimated using the new Reference-Composition Salinity Scale (Millero et al., 2008). Thermodynamic properties of seawater can be computed from the Gibbs function and its partial derivatives using the relations given in Tables 17 and 18. Thermodynamic properties of the phase transitions of seawater can be obtained in combination with the thermodynamic potentials of ice (IAPWS, 2006) and of vapour (IAPWS, 1996), Eqs. (6.25) and (6.34).

The Gibbs function consists of three parts as indicated in Fig. 8, a pure-water part (regions D and E), a normal-pressure saline part (region C), and a pressure-dependent saline part (regions A and B).

The pure-water part (D and E) is defined by the IAPWS-95 formulation (IAPWS, 1996) in the form of a Helmholtz potential, $f(T, \rho)$, where density ρ is an independent variable rather than pressure p . Conversion formulas from partial derivatives of the Helmholtz function to partial derivatives of the Gibbs function are provided in Table 2. Source code implementing the Releases of IAPWS (1996) for fluid water and of IAPWS (2006) for ice is available from the digital supplement of Feistel et al. (2008b).

For the pure-water part in the regions A and B, i.e. their intersections with the regions D and E in Fig. 8, an accurate Gibbs function approximation to IAPWS-95 is

available from the pure-water part of the 2003 Gibbs function (Feistel, 2003), and corresponding source code is provided by Feistel (2005) and Feistel et al. (2008b).

The saline part of the Gibbs function, g^S , is the polynomial-like expression (5.4) with the coefficients provided in Table 17.

The validity of the pressure-dependent part (regions A and B) is restricted to the oceanographic standard range. Properties accurately available in these regions include those derived from pressure derivatives of the Gibbs function, e.g. density and sound speed.

At normal pressure (region C), g^S covers the extended range of thermal and colligative properties up to hot and concentrated seawater. Quantities determined from pressure derivatives (e.g., density) in this region are extrapolated from the formulas given for the regions A, B, D and E and have larger uncertainties, as described in Section 7.

While this paper is focussed on the construction and basic properties of the Gibbs potential, two companion papers by McDougall et al. (2008) and Feistel et al. (2008a) will provide more details about its oceanographic application and simplified algorithms tailored for particular purposes.

This paper, in conjunction with the ones of Millero et al. (2008), McDougall et al. (2008) and Feistel et al. (2008a), together with the fluid-water properties described by Wagner and Pruß (2002), and ice by Feistel and Wagner (2006) forms a comprehensive and consistent description of thermodynamic properties of seawater, including freezing and evaporation phase transitions (Feistel et al., 2008c).

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Appendix A

A.1. Fundamental constants

Following the recommendation of IAPWS (2005), the values of the fundamental constants were taken

Table 13
Fundamental constants from CODATA 2002 (Mohr and Taylor, 2005) and ISO (1993a)

Symbol	Value	Uncertainty	Unit	Comment
N_A	6.0221415×10^{23}	0.0000010×10^{23}	mol^{-1}	Avogadro constant
k	$1.3806505 \times 10^{-23}$	$0.0000024 \times 10^{-23}$	J K^{-1}	Boltzmann constant
R	8.314472	0.000015	$\text{J mol}^{-1} \text{K}^{-1}$	Molar gas constant $R = k \times N_A$
c	299 792 458	Exact	m s^{-1}	Vacuum light speed
e	$1.60217653 \times 10^{-19}$	$0.00000014 \times 10^{-19}$	C	Elementary charge
π	3.141592653...	Exact	–	Number Pi
ϵ_0	$8.854187817 \dots \times 10^{-12}$	Exact	F m^{-1}	Electric constant $\epsilon_0 = 10^7 \text{ m H}^{-1}/(4\pi c^2)$
P_0	101 325	Exact	Pa	Normal pressure
T_0	273.15	Exact	K	Celsius zero point

Table 14
Selected properties of liquid water from IAPWS (1996, 1997, 2005, 2006) and Feistel (2003)

Symbol	Value	Uncertainty	Unit	Comment
M_W	18.015268	0.000002	g mol^{-1}	Molar mass
T_{MD}	3.978121	0.04	$^{\circ}\text{C}$	Maximum density temperature
ρ_{MD}	999.97495	0.00084	kg m^{-3}	Maximum density at P_0
ρ^0	999.8431	0.001	kg m^{-3}	Density at T_0 and P_0 , $\rho^0 = 1/\nu^0$
$(\partial\rho^0/\partial T)_P$	6.774876×10^{-2}	0.06×10^{-2}	$\text{kg m}^{-3} \text{K}^{-1}$	$(\partial\rho/\partial T)_P$ at T_0 and P_0
T_t	273.16	Exact	K	Triple point temperature
P_t	611.657	0.01	Pa	Triple point pressure
ρ_t	999.793	0.01	kg m^{-3}	Triple point density
s_t	0	Exact	$\text{J kg}^{-1} \text{K}^{-1}$	Triple point entropy
u_t	0	Exact	J kg^{-1}	Triple point internal energy
T_f^0	273.152519	0.000002	K	Freezing point at P_0
T_c	647.096	0.01	K	Critical temperature
P_c	22.064	0.0077	MPa	Critical pressure
ρ_c	322	3	kg m^{-3}	Critical density
ϵ^0	87.903455	0.04	–	Permittivity at T_0 and P_0
$(\partial\epsilon^0/\partial T)_P$	–0.4025705	0.002	K^{-1}	Temperature derivative of ϵ^0

Table 15
The sea salt composition definition for reference salinity of the standard ocean at 25 $^{\circ}\text{C}$ and 101 325 Pa

Solute j	Z_j	M_j (g mol^{-1})	X_j (10^{-7})	$X_j \times Z_j$ (10^{-7})	W_j
Na^+	+1	22.98976928(2)	4 188 071	4 188 071	0.3065958
Mg^{2+}	+2	24.3050(6)	471 678	943 356	0.0365055
Ca^{2+}	+2	40.078(4)	91 823	183 646	0.0117186
K^+	+1	39.0983(1)	91 159	91 159	0.0113495
Sr^{2+}	+2	87.62(1)	810	1620	0.0002260
Cl^-	–1	35.453(2)	4 874 839	–4 874 839	0.5503396
SO_4^{2-}	–2	96.0626(50)	252 152	–504 304	0.0771319
HCO_3^-	–1	61.01684(96)	15 340	–15 340	0.0029805
Br^-	–1	79.904(1)	7520	–7520	0.0019134
CO_3^{2-}	–2	60.0089(10)	2134	–4268	0.0004078
B(OH)_4^-	–1	78.8404(70)	900	–900	0.0002259
F^-	–1	18.9984032(5)	610	–610	0.0000369
OH^-	–1	17.00733(7)	71	–71	0.0000038
B(OH)_3	0	61.8330(70)	2807	0	0.0005527
CO_2	0	44.0095(9)	86	0	0.0000121
Sum			10 000 000	0	1.0

X —mole fractions, Z —valences, W —mass fractions (Millero et al., 2008). Molar masses M from Wieser (2006) with their uncertainties given in the brackets.

from CODATA 2002 (Mohr and Taylor 2005), as listed in Table 13.

Selected properties of pure water were taken from IAPWS (1996, 1997, 2005, 2006) as listed in Table 14. A

more recent paper (Hamelin et al., 1998) for the dielectric constant, ϵ , is not used here because its range of validity does not include 0 $^{\circ}\text{C}$, although the difference at 0 $^{\circ}\text{C}$ between ϵ from this formulation and from IAPWS (1997)

is well within the uncertainty estimate in Table 13. The difference at 0 °C between $(\partial\varepsilon/\partial T)_p$ from this formulation and from IAPWS (1997) was taken for the uncertainty estimate in Table 13. The chemical reference composition of seawater from Millero et al. (2008) is given in Table 15. Selected seawater constants derived from the reference composition are listed in Table 16.

A.2. Coefficients of the saline Gibbs function of seawater

See Table 17.

A.3. Thermodynamic relations

See Tables 18–20.

A.4. Numerical checkvalues

Check values from a double-precision implementation are reported in Tables 21 and 22. In a separate paper (Feistel et al., 2008c), corresponding values are reported with 20 significant digits from a quadruple-precision

Table 16
Selected properties of the KCl-normalized reference seawater (Millero et al., 2008), and proposals of the WG127 (2006)

Symbol	Value	Uncertainty	Unit	Comment
M_S	31.4038218	0.001	g mol^{-1}	Reference salinity molar mass $M_S = \sum_j X_j M_j$
Z^2	1.2452898	Exact ^a	–	Reference salinity valence factor $Z^2 = \sum_j X_j Z_j^2$
N_S	1.9176461×10^{22}	6×10^{17}	g^{-1}	Reference salinity particle number $N_S = N_A/M_S$
u_{PS}	1.004715...	Exact ^a	g kg^{-1}	Unit conversion factor, $35.16504 \text{ g kg}^{-1}/35$
S_{SO}	35.16504	Exact ^a	g kg^{-1}	Standard ocean reference salinity, $35 u_{PS}$
T_{SO}	273.15	Exact	K	Standard ocean temperature $T_{SO} = T_0$
t_{SO}	0	Exact	°C	Standard ocean temperature $t_{SO} = T_{SO} - T_0$
P_{SO}	101325	Exact	Pa	Standard ocean surface pressure $P_{SO} = P_0$
p_{SO}	0	Exact	Pa	Standard ocean surface sea pressure $p_{SO} = P_{SO} - P_0$
h_{SO}	0	Exact	J kg^{-1}	Standard ocean surface enthalpy $h_{SO} = u_t$
s_{SO}	0	Exact	$\text{J kg}^{-1} \text{K}^{-1}$	Standard ocean surface entropy $s_{SO} = s_t$
S_u	40.188617...	Exact ^a	g kg^{-1}	Unit-related scaling constant, $40 u_{PS}$
t_u	40	Exact	°C	Unit-related scaling constant
p_u	10^8	Exact	Pa	Unit-related scaling constant
g_u	1	Exact	J kg^{-1}	Unit-related scaling constant

^a By definition of reference salinity and reference composition.

Table 17
Non-zero coefficients g_{ijk} of the saline specific Gibbs energy $g^S(S_A, t, p)$ as a function of the independent variables absolute salinity, $S_A = S_u \times x^2$, ITS-90 Celsius temperature, $t = t_u \times y$, and sea pressure, $p = p_u \times z$

i	j	k	g_{ijk}	i	j	k	g_{ijk}	i	j	k	g_{ijk}
1	0	0	5812.81456626732	2	5	0	-21.6603240875311	3	2	2	-54.1917262517112
1	1	0	851.226734946706	4	5	0	2.49697009569508	2	3	2	-204.889641964903
2	0	0	1416.27648484197	2	6	0	2.13016970847183	2	4	2	74.726141138756
3	0	0	-2432.14662381794	2	0	1	-3310.49154044839	2	0	3	-96.5324320107458
4	0	0	2025.80115603697	3	0	1	199.459603073901	3	0	3	68.0444942726459
5	0	0	-1091.66841042967	4	0	1	-54.7919133532887	4	0	3	-30.1755111971161
6	0	0	374.601237877840	5	0	1	36.0284195611086	2	1	3	124.687671116248
7	0	0	-48.5891069025409	2	1	1	729.116529735046	3	1	3	-29.483064349429
2	1	0	168.072408311545	3	1	1	-175.292041186547	2	2	3	-178.314556207638
3	1	0	-493.407510141682	4	1	1	-22.6683558512829	3	2	3	25.6398487389914
4	1	0	543.835333000098	2	2	1	-860.764303783977	2	3	3	113.561697840594
5	1	0	-196.028306689776	3	2	1	383.058066002476	2	4	3	-36.4872919001588
6	1	0	36.7571622995805	2	3	1	694.244814133268	2	0	4	15.8408172766824
2	2	0	880.031352997204	3	3	1	-460.319931801257	3	0	4	-3.41251932441282
3	2	0	-43.0664675978042	2	4	1	-297.728741987187	2	1	4	-31.656964386073
4	2	0	-68.5572509204491	3	4	1	234.565187611355	2	2	4	44.2040358308
2	3	0	-225.267649263401	2	0	2	384.794152978599	2	3	4	-11.1282734326413
3	3	0	-10.0227370861875	3	0	2	-52.2940909281335	2	0	5	-2.62480156590992
4	3	0	49.3667694856254	4	0	2	-4.08193978912261	2	1	5	7.04658803315449
2	4	0	91.4260447751259	2	1	2	-343.956902961561	2	2	5	-7.92001547211682
3	4	0	0.875600661808945	3	1	2	83.1923927801819				
4	4	0	-17.1397577419788	2	2	2	337.409530269367				

The saline Gibbs function is computed from $g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ g_{1jk} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j z^k$.

Coefficients with $k > 0$ are adopted from Feistel (2003). Pure-water coefficients with $i = 0$ do not occur in the saline contribution.

Table 18

Relations of the thermodynamic properties to the equation for the Gibbs energy and its temperature and pressure derivatives^a

Property	Relation	Unit
<i>Density</i>		
$\rho(t, p) = v^{-1} = (\partial g / \partial p)_t^{-1}$	$\rho(t, p) = g_p^{-1}$	kg m ⁻³
<i>Specific entropy</i>		
$s(t, p) = -(\partial g / \partial t)_p$	$s(t, p) = -g_t$	J kg ⁻¹ K ⁻¹
<i>Specific enthalpy</i>		
$h(t, p) = g + Ts$	$h(t, p) = g - Tg_t$	J kg ⁻¹
<i>Specific internal energy</i>		
$u(t, p) = g + Ts - Pv$	$u(t, p) = g - Tg_t - Pg_p$	J kg ⁻¹
<i>Specific Helmholtz energy</i>		
$f(t, p) = g - Pv$	$f(t, p) = g - Pg_p$	J kg ⁻¹
<i>Specific isobaric heat capacity</i>		
$c_p(t, p) = T(\partial s / \partial t)_p$	$c_p(t, p) = -Tg_{tt}$	J kg ⁻¹ K ⁻¹
<i>Specific isochoric heat capacity</i>		
$c_v(t, \rho) = T(\partial s / \partial t)_v$	$c_v(t, \rho) = T(g_{tp}^2 - g_{tt}g_{pp})/g_{pp}$	J kg ⁻¹ K ⁻¹
<i>Thermal expansion coefficient</i>		
$\alpha(t, p) = v^{-1}(\partial v / \partial t)_p$	$\alpha(t, p) = g_{tp}/g_p$	1 K ⁻¹
<i>Isothermal compressibility</i>		
$\kappa_T(t, p) = -v^{-1}(\partial v / \partial p)_t$	$\kappa_T(t, p) = -g_{pp}/g_p$	1 Pa ⁻¹
<i>Isentropic compressibility</i>		
$\kappa_s(t, p) = -v^{-1}(\partial v / \partial p)_s$	$\kappa_s(t, p) = (g_{tp}^2 - g_{tt}g_{pp})/(g_p g_{tt})$	1 Pa ⁻¹
<i>Sound speed</i>		
$c(t, p) = \sqrt{(\partial p / \partial \rho)_s}$	$c(t, p) = g_p \sqrt{g_{tt}/(g_{tp}^2 - g_{tt}g_{pp})}$	m s ⁻¹
<i>Adiabatic lapse rate</i>		
$\Gamma(t, \rho) = (\partial t / \partial p)_s$	$\Gamma(t, \rho) = -g_{tp}/g_{tt}$	K Pa ⁻¹

^a $g_t \equiv [\partial g / \partial t]_{s,p}$, $g_p \equiv [\partial g / \partial p]_{s,t}$, $g_{tt} \equiv [\partial^2 g / \partial t^2]_{s,p}$, $g_{tp} \equiv [\partial^2 g / \partial t \partial p]_{s,p}$, $g_{pp} \equiv [\partial^2 g / \partial p^2]_{s,t}$.

Table 19

Relations of the thermodynamic properties to the equation for the Gibbs energy of seawater, Eq. (5.1), and its salinity and pressure derivatives^a

Property	Relation	Unit
<i>Relative chemical potential</i>		
$\mu(S_A, t, p) = (\partial g / \partial S_A)_{t,p}$	$\mu(S_A, t, p) = g_s$	J g ⁻¹
<i>Chemical potential of water</i>		
$\mu^W(S_A, t, p) = g - S_A \mu$	$\mu^W(S_A, t, p) = g - S_A g_s$	J kg ⁻¹
<i>Chemical potential of sea salt</i>		
$\mu^S = \mu + \mu^W$	$\mu^S(S_A, t, p) = g + (1 - S_A)g_s$	J kg ⁻¹
<i>Osmotic coefficient</i>		
$\phi(S_A, t, p) = (g^W - \mu^W)/(mRT)$	$\phi(S_A, t, p) = -(g^S - S_A g_s)/(mRT)$	1
<i>Haline contraction coefficient</i>		
$\beta(S_A, t, p) = \rho^{-1}(\partial \rho / \partial S_A)_{t,p}$	$\beta(S_A, t, p) = -g_{sp}/g_p$	kg g ⁻¹
<i>Barodiffusion ratio</i>		
$k_p(S_A, t, p) = p(\partial v / \partial S_A)_{t,p} / (\partial \mu / \partial S_A)_{t,p}$	$k_p(S_A, t, p) = pg_{sp}/g_{ss}$	g kg ⁻¹

^a $g_s \equiv [\partial g / \partial S_A]_{t,p}$, $g_p \equiv [\partial g / \partial p]_{s,t}$, $g_{sp} \equiv [\partial^2 g / \partial S_A \partial p]_{t,p}$, $m = (1/M_S)(S_A/(1 - S_A))$ is the molality.

Table 20

Relations of the thermodynamic properties to the equation for the Helmholtz energy and its temperature and density derivatives^a

Property	Relation	Unit
<i>Pressure</i>		
$P(T, \rho) = -(\partial f / \partial v)_T$	$P(T, \rho) = \rho^2 f_\rho$	Pa
<i>Specific entropy</i>		
$s(T, \rho) = -(\partial f / \partial T)_\rho$	$s(T, \rho) = -f_T$	J kg ⁻¹ K ⁻¹
<i>Specific enthalpy</i>		
$h(T, \rho) = f + Ts + Pv$	$h(T, \rho) = f - Tf_T + \rho f_\rho$	J kg ⁻¹
<i>Specific internal energy</i>		
$u(T, \rho) = f + Ts$	$u(T, \rho) = f - Tf_T$	J kg ⁻¹
<i>Specific Gibbs energy</i>		
$g(T, \rho) = f + Pv$	$g(T, \rho) = f + \rho f_\rho$	J kg ⁻¹
<i>Specific isochoric heat capacity</i>		
$c_v(T, \rho) = T(\partial s / \partial T)_\rho$	$c_v(T, \rho) = -Tf_{TT}$	J kg ⁻¹ K ⁻¹

Table 20 (continued)

Property	Relation	Unit
Specific isobaric heat capacity $c_p(T, \rho) = T(\partial s/\partial T)_p$	$c_p(T, \rho) = T \left(\frac{\rho f_{T\rho}^2}{2f_\rho + \rho f_{\rho\rho}} - f_{TT} \right)$	$\text{J kg}^{-1} \text{K}^{-1}$
Isothermal compressibility $\kappa_T(T, \rho) = (1/\rho)(\partial \rho/\partial P)_T$	$\kappa_T(T, \rho) = \frac{1}{\rho^2(2f_\rho + \rho f_{\rho\rho})}$	Pa^{-1}
Isentropic compressibility $\kappa_s(T, \rho) = (1/\rho)(\partial \rho/\partial P)_s$	$\kappa_s(T, \rho) = \frac{f_{TT}/\rho^2}{f_{TT}(2f_\rho + \rho f_{\rho\rho}) - \rho f_{T\rho}^2}$	Pa^{-1}
Thermal expansion coefficient $\alpha(T, \rho) = -(1/\rho)(\partial \rho/\partial T)_p$	$\alpha(T, \rho) = \frac{f_{T\rho}}{2f_\rho + \rho f_{\rho\rho}}$	K^{-1}
Sound speed $c(T, \rho) = \sqrt{(\partial P/\partial \rho)_s}$	$c(T, \rho) = \sqrt{\rho^2 \frac{f_{TT} f_{\rho\rho} - f_{T\rho}^2}{f_{TT}} + 2\rho f_\rho}$	m s^{-1}
Adiabatic lapse rate $\Gamma(T, \rho) = (\partial T/\partial P)_s$	$\Gamma(T, \rho) = \frac{f_{T\rho}/\rho}{\rho f_{T\rho}^2 - f_{TT}(2f_\rho + \rho f_{\rho\rho})}$	K Pa^{-1}

^a $f_T \equiv [\partial f/\partial T]_p, f_\rho \equiv [\partial f/\partial \rho]_T, f_{TT} \equiv [\partial^2 f/\partial T^2]_p, f_{T\rho} \equiv [\partial^2 f/\partial T \partial \rho], f_{\rho\rho} \equiv [\partial^2 f/\partial \rho^2]_T.$

Table 21
Properties usable as numerical check values

Quantity	Value	Value	Value	Unit
S_A	35.16504	100	35.16504	g kg^{-1}
t	0.0	79.85	0.0	$^\circ\text{C}$
p	0.0	0.0	99.898675×10^6	Pa
g	0.0	-0.295243229×10^5	0.951294557×10^5	J kg^{-1}
$(\partial g/\partial S_A)_{t,p}$	0.639974067×10^2	0.251957276×10^3	-0.545861581×10	J g^{-1}
$(\partial g/\partial t)_{s,p}$	0.0	-0.917529024×10^3	0.160551219×10^2	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial g/\partial p)_{s,t}$	$0.972661217 \times 10^{-3}$	$0.971006828 \times 10^{-3}$	$0.933770945 \times 10^{-3}$	$\text{m}^3 \text{kg}^{-1}$
$(\partial^2 g/\partial S_A \partial p)_{t,p}$	$-0.759615412 \times 10^{-6}$	$-0.305957802 \times 10^{-6}$	$-0.640757619 \times 10^{-6}$	$\text{m}^3 \text{g}^{-1}$
$(\partial^2 g/\partial t^2)_{s,p}$	-0.145944931×10^2	-0.106092735×10^2	-0.138089104×10^2	$\text{J kg}^{-1} \text{K}^{-2}$
$(\partial^2 g/\partial t \partial p)_{s,t}$	$0.515167556 \times 10^{-7}$	$0.146211315 \times 10^{-5}$	$0.245708012 \times 10^{-6}$	$\text{m}^3 \text{kg}^{-1} \text{K}^{-1}$
$(\partial^2 g/\partial p^2)_{s,t}$	$-0.450775377 \times 10^{-12}$	$-0.261586665 \times 10^{-12}$	$-0.335796316 \times 10^{-12}$	$\text{m}^3 \text{kg}^{-1} \text{Pa}^{-1}$
h	0.0	0.294363423×10^6	0.907439992×10^5	J kg^{-1}
f	-0.985548978×10^2	-0.296227102×10^5	0.175236121×10^4	J kg^{-1}
u	-0.985548978×10^2	0.294265035×10^6	-0.263309532×10^4	J kg^{-1}
s	0.0	0.917529024×10^3	-0.160551219×10^2	$\text{J kg}^{-1} \text{K}^{-1}$
ρ	0.102810720×10^4	0.102985888×10^4	0.107092645×10^4	kg m^{-3}
c_p	0.398648579×10^4	0.374507355×10^4	0.377190387×10^4	$\text{J kg}^{-1} \text{K}^{-1}$
c	0.144900246×10^4	0.396127835×10^4	0.162198998×10^4	m s^{-1}
μ^w	-0.225047137×10^4	-0.547200505×10^5	0.953214082×10^5	J kg^{-1}

Note that some check values are located in regions (C) and (F) of Fig. 8, i.e. extrapolated from the validity region with significant uncertainties, like e.g. sound speed c in the middle column.

Table 22
Zero-salinity properties corresponding to the check values given in Table 21

Quantity	Value	Value	Value	Unit
S_A	0.0	0.0	0.0	g kg^{-1}
t	0.0	79.85	0.0	$^\circ\text{C}$
p	0.0	0.0	99.898675×10^6	Pa
g	0.101342742×10^3	-0.446114969×10^5	0.977303862×10^5	J kg^{-1}
$(\partial g^w/\partial S_A)_{t,p}$	0.0	0.0	0.0	J g^{-1}
$(\partial g/\partial t)_{s,p}$	0.147643376	-0.107375993×10^4	0.851466502×10	$\text{J kg}^{-1} \text{K}^{-1}$
$(\partial g/\partial p)_{s,t}$	$0.100015694 \times 10^{-2}$	$0.102892956 \times 10^{-2}$	$0.956683329 \times 10^{-3}$	$\text{m}^3 \text{kg}^{-1}$
$(\partial^2 g/\partial S_A \partial p)_{t,p}$	0.0	0.0	0.0	$\text{m}^3 \text{g}^{-1}$
$(\partial^2 g/\partial t^2)_{s,p}$	-0.154473542×10^2	-0.118885000×10^2	-0.142969873×10^2	$\text{J kg}^{-1} \text{K}^{-2}$
$(\partial^2 g/\partial t \partial p)_{s,t}$	$-0.677700318 \times 10^{-7}$	$0.659051552 \times 10^{-6}$	$0.199079571 \times 10^{-6}$	$\text{m}^3 \text{kg}^{-1} \text{K}^{-1}$
$(\partial^2 g/\partial p^2)_{s,t}$	$-0.508928895 \times 10^{-12}$	$-0.474672819 \times 10^{-12}$	$-0.371530889 \times 10^{-12}$	$\text{m}^3 \text{kg}^{-1} \text{Pa}^{-1}$
h	0.610139535×10^2	0.334425759×10^6	0.954046055×10^5	J kg^{-1}
f	0.18399×10^{-2}	-0.447157532×10^5	0.206205330×10^4	J kg^{-1}
u	-0.403269484×10^2	0.334321503×10^6	-0.263727446×10^3	J kg^{-1}

Table 22 (continued)

Quantity	Value	Value	Value	Unit
s	−0.147643376	0.107375993×10^4	$−0.851466502 \times 10$	$\text{J kg}^{-1} \text{K}^{-1}$
ρ	0.999843086×10^3	0.971883832×10^3	0.104527796×10^4	kg m^{-3}
c_p	0.421944481×10^4	0.419664050×10^4	0.390522209×10^4	$\text{J kg}^{-1} \text{K}^{-1}$
c	0.140238253×10^4	0.155446297×10^4	0.157542240×10^4	m s^{-1}
μ^w	0.101342742×10^3	$−0.446114969 \times 10^5$	0.977303862×10^5	J kg^{-1}

At $S_A = 0$, the saline Gibbs function g^s and its derivatives are zero except for $(\partial g^s / \partial S_A)_{T,p}$ which shows a singularity.

implementation, with estimates for their digit numbers reproducible in double-precision code.

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