THERMODYNAMIC PROPERTIES OF SEAWATER

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Contents

Summary

The International Thermodynamic Equation of Seawater 2010, TEOS-10, is the latest oceanographic standard formulation for the thermodynamic properties of Standard Seawater as specified and distributed by IAPSO, the International Association for the Physical Sciences of the Oceans. In this chapter it is briefly outlined how TEOS-10 describes seawater and its equilibria with liquid water, ice, water vapor and humid air. The scales are explained on which temperature and salinity are expressed within TEOS-10, as well as the reference state conditions used to specify the absolute values of energy and entropy of water, sea salt, and dry air. In the end, selected seawater properties derived from TEOS-10 are displayed graphically.

1. Introduction

Water is the very key substance for our biological existence as individuals, for our private daily life cycle, for the processes in agriculture and industry, as well as in our environment and in the climate system with oceans, rivers, humid air and clouds. As a pure substance under ambient conditions, water occurs in three thermodynamic phases, as gaseous water vapor, as liquid water, and as solid ice with a hexagonal crystal lattice, termed ice Ih. In the atmosphere, water vapor is mixed with several gases jointly referred to as “dry air”. In the oceans, several salts are dissolved in water, forming a mixture known as “sea salt”. Water is also present as moisture in soil and rocks, and is taken up, stored and released by plants and animals. Ranking second behind radiation energy, the latent heat transferred by water between ocean and atmosphere, released in clouds or consumed by melting glaciers is controlling climate and weather dynamics.

Satellites, radiosondes, meteorological stations, research vessels (Figure 1) and automatic buoys are used to provide observational data for pressure, temperature, humidity and salinity of the atmosphere, the hydrosphere and the cryosphere at certain points in space and time. The measuring instruments are calibrated with respect to international metrological standards to ensure temporal and spatial comparability of the various measurement results. Those metrological standards are gradually improving with respect to their uncertainty, consistency and stability. If (and only if) common calibration standards are used for field measurements and in the laboratory, the results of precision experiments to determine, say, the density of humid air or the heat capacity of seawater, can be used for the computation of related thermodynamic properties for the real atmosphere and ocean from temperature, humidity and salinity readings. For this purpose, equations of state for the particular substances are developed from laboratory data, and later evaluated frequently with field data taken as input parameters. It is obvious that those computed properties, such as the local density of the ocean or the dewpoint of air, are comparable for different times (over centuries) and locations (on the global scale) only if consistent equations and measuring standards are employed. In the Sections 2 and 3, the metrological background of temperature and salinity measurements is briefly addressed. With its focus on seawater, this chapter describes the current state of the art regarding those equations available for geosciences and climatology. The recent oceanographic formulation TEOS-10 (IOC et al., 2010), the Thermodynamic Equation of Seawater 2010, offers significant progress towards an internationally recognized general standard on thermodynamic properties of geophysical fluids even though various problems are still challenging (WMO, 2010), see Section 8.

Because of permanent intense exchange of energy and matter between atmosphere, hydrosphere and cryosphere, a comprehensive, consistent description of seawater thermodynamics must include the colligative properties of the phase transitions such as freezing point and melting heat, or vapor pressure and latent heat of evaporation in the presence of air and sea salt. For this reason, the TEOS-10 equation of state for seawater, Section 5, is accompanied by related equations for ice and humid air. The substances involved are pure water (in its three phases, as specified in Sections 5 and 6), sea salt (Section 5) and dry air (Section 7), in conjunction with the scales used to measure in practice the composition of the particular mixture.

Traditionally, thermodynamic properties of seawater, ice and humid air are described by collections of separate correlation equations for a number of relevant properties, such as functions providing values for the density, the heat capacity or the sound speed (Gill, 1982; Fofonoff and Millard, 1983; Siedler and Peters, 1986; Mamayev et al., 1991; Petrenko and Whitworth, 1999; Millero, 2001; Jacobson, 2005; Murphy and Koop, 2005; Sharqawya et al., 2010; Feistel et al., 2010a). Such collections are usually incomplete, their mutual consistency is uncertain, ranges of validity and uncertainty are often insufficiently known, thermodynamic reference states are rarely specified, and temperature scales may be obsolete or not even reported. The history of equations of state for seawater is reviewed by Millero (2010).

Figure 1. Conductivity-Temperature-Depth bathysonde (CTD) lowered into the Baltic Sea for reading the local vertical profile of seawater properties. Photo taken on 25 March 2010 onboard of r/v “Prof. A. Penck”.

To overcome most of those problems, TEOS-10 is basically composed of four independent but mutually consistent thermodynamic potentials, as shown schematically in Figure 2, for (i) fluid water, (ii) ice Ih, (iii) sea salt dissolved in liquid water, and (iv) dry air mixed with water vapor.

A *thermodynamic potential*, also termed *fundamental equation of state*, is a single function from which all the equilibrium properties of a given thermodynamic system can consistently be computed, with the exception of interface properties such as surface tension. Transport properties such as electric or thermal conduction do not belong to the thermodynamic properties. The existence of thermodynamic potentials was discovered already by Gibbs (1873); methods of their practical use are reviewed by Tillner-Roth (1998) and Alberty (2001). For seawater, Fofonoff (1962) discussed the mathematical relations between the potential function and measurable oceanographic properties, but later this theoretical option was mentioned only exceptionally in textbooks or university courses on oceanography. For practical use, the first potential function of seawater was quantitatively determined by Feistel (1993), constructed consistently with the previous 1980 International Equation of State of Seawater, EOS-80.

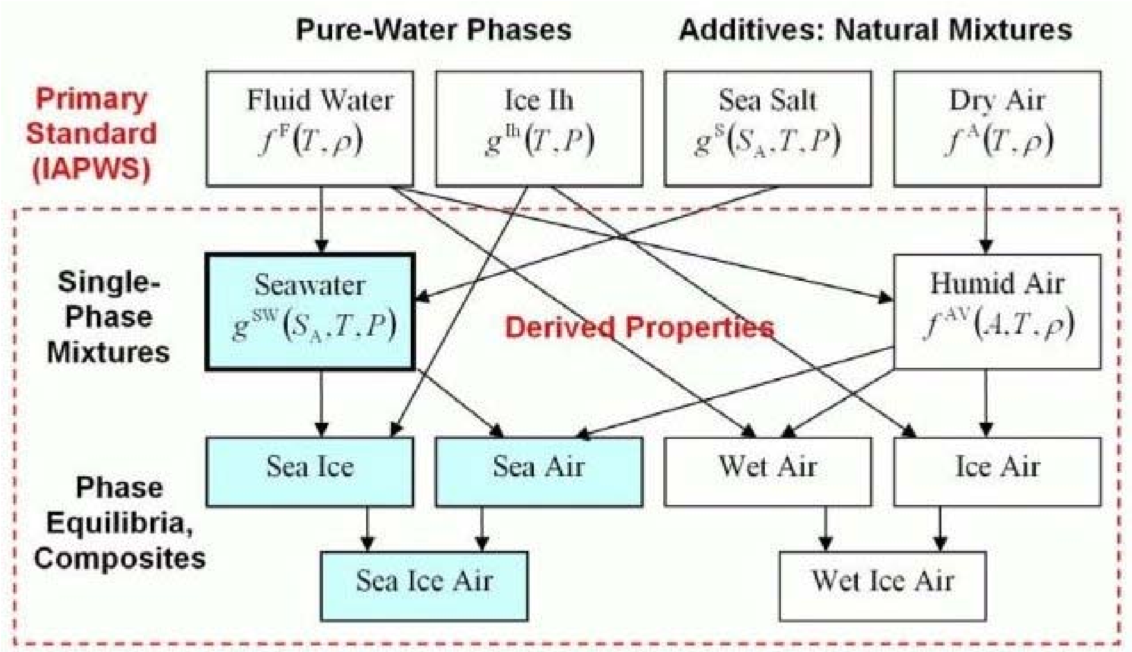

Figure 2. Schematic of the building-block structure of TEOS-10. Its Primary Standard (top row) consists of four independent and consistent thermodynamic potentials, formulated as documents of the International Association for the Properties of Water and Steam (IAPWS). From those equations, all the thermodynamic properties of liquid water, water vapor, ice, seawater and humid air, their mutual phase equilibria and composites can be computed by purely mathematical procedures without additional empirical constants or formulas.

For different sets of requisite independent variables, suitable alternative thermodynamic potentials can be chosen. They are physically and mathematically equivalent, the choice between them depends on purpose and convenience. Most frequently used are Gibbs functions, g, depending on temperature and pressure, and Helmholtz functions, f, depending on temperature and density, see Figure 2. Another important potential function is enthalpy, h, expressed in terms of entropy and pressure (Feistel and Hagen, 1995). Gibbs functions are most convenient because temperature and pressure are directly measurable input parameters; a technical drawback of Gibbs functions is that they are multi-valued in the vicinity of phase transitions (Kittel, 1969). Helmholtz functions are unique even in the vicinity of a critical point and are therefore preferred for fluids such as water if a wide range of conditions is to be covered. Moreover, Helmholtz functions are strictly additive for mixtures of ideal gases. In contrast, enthalpy is a very convenient function for the description of adiabatic processes; thermal isolation of a given fluid parcel is often observed in good approximation in oceanography and meteorology. For this purpose, potential temperature or conservative temperature may be used as independent thermal variable rather than in-situ temperature (IOC et al., 2010).

For the practical computation of properties from the thermodynamic potentials, the Seawater-Ice-Air (SIA) Library of TEOS-10 is organized in Levels 0-5, see Figure 2. Level 0 contains supplementary physical constants and auxiliary mathematical procedures. The IAPWS formulations of the thermodynamic potentials (IAPWS 2008, 2009a, 2009b, 2010a) form the library Level 1, termed the Primary Standard of TEOS-10. They obey the axiomatic principles of consistency, independence and completeness (Feistel et al., 2008a). Consistency means that it is impossible to derive different formulas for one and the same property. Independence expresses the fact that it is impossible to derive the same formula from two different parts of the formulation. Finally, completeness indicates that all the thermodynamic properties of the pure phases, their mixtures and composites can be computed from the Primary Standard by purely mathematical or numerical manipulations. Reference states used to unambiguously specify the thermodynamic potentials are explained in Section 4. Thus, Level 1 contains the entire set of empirical coefficients which in a compact form express the quantitative knowledge gained from numerous laboratory experiments; updating Level 1 in part or as a whole will automatically update all other computed properties except those available from Level 5 and from the Gibbs Seawater (GSW) Library of TEOS-10.

Level 2 provides properties of pure phases and mixtures directly available from Level 1 functions by partial derivatives and algebraic combinations. At Level 3, alternative independent variables are introduced by means of numerical iteration procedures to invert the algebraic equations. At Level 4, properties of phase equilibria and composite systems are derived from Levels 1-3. Finally, Level 5 contains additional correlation functions determined by regression with respect to data points computed from Levels 1-4. Level 5 functions are usually optimized for computation speed at the cost of accuracy or range of validity. A detailed overview over the thermodynamic properties available and the algorithms used at the different levels is given by Feistel et al. (2009a), Wright et al. (2009a), and McDougall and Barker (2011).

The latest version of the TEOS-10 Manual, the latest library implementation and the most relevant background papers are freely available from the website www.teos-10.org

The four IAPWS formulations, see Figure 2, are freely available from the website www.iapws.org. The explicit mathematical expressions and the sets of empirical coefficients of the thermodynamic potentials are available from the documents provided on those web sites; in this chapter we refrain from presenting the numerical details.

2. Temperature Scale

Definition and measurement of temperature is a scientifically and metrologically demanding task. On the currently valid International Temperature Scale of 1990 (ITS-90), the unit kelvin (K) is defined by the condition that the temperature at the liquid-gas-solid triple point of pure water is $T_\mathrm{t} = 273.16\,\mathrm{K}$ exactly (Blanke, 1989; Preston-Thomas, 1990; Rudtsch and Fischer, 2008). As already demonstrated by Galilei in 1592, most gases and liquids (such as mercury) change their volumes at constant pressure proportional to the temperature, and can be used to obtain intermediate temperature readings from length measurements between two points at which the thermometer is calibrated to certain values. Such points may be the triple points of water and of other substances. Similarly, the temperature dependence of the resistance of electric conductors (such as platinum) may be exploited to obtain temperature information from measurements of voltages or electric currents. On the other hand, certain physical laws such as the ideal-gas law for the pressure of a dilute gas or the Stefan-Boltzmann law for the thermal radiation of a black body relate the so-called “thermodynamic temperature” to other measurable physical quantities. The progress in high-precision experiments permits the detection of deviations between the theoretical thermodynamic temperature and the related temperature measured practically with calibrated thermometers (Fischer et al., 2011, see Figure 3). Thus, from time to time the metrological temperature-scale realization must be revised to improve its consistency with the thermodynamic temperature within the uncertainty of the most accurate experiments. The most important precursor scales of ITS-90 where those of 1948 (IPTS-48) and 1968 (IPTS-68).

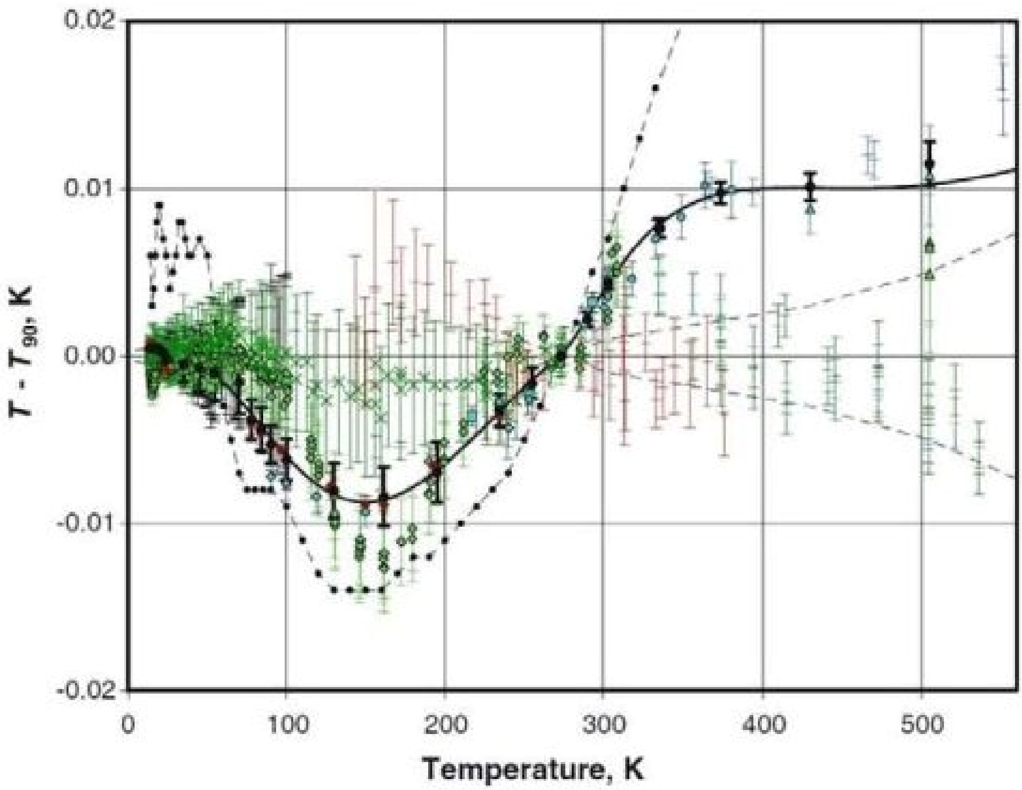

Figure 3. Deviation of the currently best estimate for the thermodynamic temperature, T, shown as the bold curve, from the temperature T_{90} expressed on the current International Temperature Scale of 1990, ITS-90. The two symmetric dotted curves represent the measurement uncertainty of ITS-90. The dotted curve connecting bigger dots shows the deviation of the previous temperature scale of 1968, IPTS-68, from ITS-90. Additionally, results of various precision measurements are shown with error bars. Diagram adapted from Fischer et al. (2011), courtesy of Joachim Fischer.

In oceanography, the accuracy requirements for temperature measurements are very high, even under the harsh conditions at sea. In the most relevant range between 270 K and 300 K, the deviation between ITS-90 and IPTS-68 must not be neglected (Saunders, 1990, see also Figure 3). While modern instruments such as a CTD (see Figure 1) report temperatures on ITS-90, most precision measurements of seawater properties were carried out with respect to meanwhile obsolete scales. In particular, the previous

International Equation of State of Seawater 1980 (EOS-80) and the Practical Salinity Scale of 1978 (PSS-78) are specified in terms of IPTS-68. The conversion of data and formulas between temperature scales does not only include the temperature value itself, also thermal properties such as heat capacities were properly corrected to ITS-90 for the construction of TEOS-10 (Rusby, 1991; Goldberg and Weir, 1992; Feistel, 2008a).

A redefinition of the SI unit *kelvin* (K) is in preparation, among other reasons because water is actually not a pure substance with a triple "point" in the *T*-*P* diagram. Rather, the three-phase equilibrium is possible in a tiny region as a result of the presence of different isotopes of hydrogen and oxygen that are mixed in the current Vienna Standard Mean Ocean Water (VSMOW). If the isotope ratios in the different phases of water vary, the locus of the triple point is slightly displaced within an estimated range of 14 µK (Nicholas et al., 1996; White et al., 2003; Rudtsch and Fischer, 2008). In the upcoming new SI definition of temperature, one kelvin will be defined in terms of the energy unit joule, 1 J = 1 N m, by,

$$1\,\mathrm{K} = 1\,\mathrm{J}/k_\mathrm{B}, \tag{1}$$

where $k_\mathrm{B} = 1.380\ 6513(18)\times 10^{-23}\,\mathrm{J\,K^{-1}}$ is the currently best value of the Boltzmann constant to which an exact numerical value will be assigned in the near future (Fellmuth, 2003; Quinn, 2007; Seidel et al., 2007; Jones, 2009; Fischer et al., 2011; BIPM, 2011). Independent of the redefinition of the kelvin, for a number of years ITS-90 is expected to remain the internationally agreed scale against which thermometers will be calibrated further on, although with an increasingly better known deviation from the thermodynamic temperature.

3. Salinity Scale

Seawater is a multi-component aqueous electrolyte solution. The salt dissolved in ocean waters is a mixture of a numerous chemical species. Almost two centuries ago (Marcet, 1819), the empirical rule was discovered that seawater properties all over the world can be described rather accurately if only the sample's temperature, pressure and chlorinity are known, ignoring any other details of the chemical composition of sea salt. Here, chlorinity (Cl) of seawater is defined as 0.3285234 times the ratio of the mass of pure silver, m_Ag, required to precipitate all dissolved ions of chloride, bromide and iodide in seawater to the mass of seawater, m_SW (Jacobsen and Knudsen, 1940; Millero et al., 2008):

$$Cl \equiv 0.3285234 \times m_\mathrm{Ag}/m_\mathrm{SW}. \tag{2}$$

In the 1960s it turned out that the ratio of the electrical conductivity of seawater to that of a reference solution of sodium chloride (KCl) can be measured as accurately but much faster and easier than chlorinity by chemical titration. Samples of Standard Seawater (SSW) were used to establish a precise empirical relationship between conductivity ratio (C) and Cl of seawater in the laboratory (Cox et al., 1967; Poisson, 1980; Culkin and Smith, 1981). The equation

$$S_P \equiv 1.80655 \times Cl\left(C,t,p\right) \big/ (\text{g kg}^{-1}) \qquad (3)$$

was then used to define Practical Salinity as a dimensionless quantity on the Practical Salinity Scale of 1978 (PSS-78) of SSW as a function of conductivity ratio, Celsius temperature t (IPTS-68), and sea pressure p, relative to atmospheric pressure (Lewis and Perkin, 1978, 1980; Lewis, 1980; UNESCO, 1981a,b). The numerical value of S_P is a fairly rough estimate for the mass fraction in g/kg of salt dissolved in SSW. Although never endorsed officially, in the oceanographic literature the unit "psu" for "Practical Salinity Unit" is often found attached to measured values in order to indicate that the given number is expressed on PSS-78. Neither PSS-78 nor "psu" are part of the International System of Units, SI (BIPM, 2006).

For absolute salinity, S_A, defined as the mass fraction of dissolved material in seawater, an estimate better than S_P can be calculated from the best available results of chemical composition analyses of SSW. In Table 1 this so-called Reference Composition is shown (Millero et al., 2008).

Solute	**Electric charge**	**Mole fraction**	**Mass fraction**	**Molar mass g mol^{-1}**
Na^+	+1	0.418 8071	0.306 5958	22.989 769 28(2)
Mg^{2+}	+2	0.047 1678	0.036 5055	24.3050(6)
Ca^{2+}	+2	0.009 1823	0.011 7186	40.078(4)
K^+	+1	0.009 1159	0.011 3495	39.0983(1)
Sr^{2+}	+2	0.000 0810	0.000 2260	87.62(1)
Cl^-	–1	0.487 4839	0.550 3396	35.453(2)
SO_4^{2-}	–2	0.025 2152	0.077 1319	96.0626(50)
HCO_3^-	–1	0.001 5340	0.002 9805	61.016 84(96)
Br^-	–1	0.000 7520	0.001 9134	79.904(1)
CO_3^{2-}	–2	0.000 2134	0.000 4078	60.0089(10)
$B(OH)_4^-$	–1	0.000 0900	0.000 2259	78.8404(70)
F^-	–1	0.000 0610	0.000 0369	18.998 403 2(5)
OH^-	–1	0.000 0071	0.000 0038	17.007 33(7)
$B(OH)_3$	0	0.000 2807	0.000 5527	61.8330(70)
CO_2	0	0.000 0086	0.000 0121	44.0095(9)
Sea salt	0	1.000 0000	1.000 0000	31.404(2)

Table 1. Chemical Reference Composition of sea salt (Millero et al., 2008). Mole fractions are exact by definition, mass fractions are rounded to seven digits behind the period and may be subject to future updates of molar masses. Uncertainties of the IUPAC molar masses (Wieser, 2006) are enclosed in brackets (BIPM, 2006; JCGM, 2008). The composition obeys exact electro-neutrality.

Summing up the molar masses of the Reference Composition constituents results in a relation between Cl, or similarly S_P, Eq. (3), and absolute salinity of seawater with

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Biographical Sketch

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