Notes on the GSW function gsw_SR_from_SP

Notes made 15th March 2011

The "raw" physical oceanographic data, as collected from ships and from autonomous platforms (e. g. ARGO), and as stored in national oceanographic data bases, are

- Practical Salinity (S_P, unitless) and
- in situ temperature (t, °C) as functions of
- pressure (p, dbar), at a series of
- longitude and latitude.

Under TEOS-10 all the thermodynamic properties are functions of Absolute Salinity S_A (rather than of Practical Salinity), hence the first step in processing oceanographic data is to calculate Absolute Salinity, and this is accomplished by the GSW function **gsw_SA_from_SP**:- note that it is not possible to calculate Conservative Temperature Θ until Absolute Salinity is first evaluated since Θ is a function of Absolute Salinity (as opposed to being a function of Practical Salinity). Hence the function **gsw_SA_from_SP**, is perhaps the most fundamental of the GSW functions as it is the gateway leading from oceanographic measurements to all the thermodynamic properties of seawater under TEOS-10. A call to **gsw_SA_from_SP** can be avoided only if one is willing to ignore the influence of the spatial variations in the composition of seawater on seawater properties (such as density and specific volume). If this is indeed the intention, then the remaining GSW functions must be called with the salinity argument being Reference Salinity S_R, not Practical Salinity S_P. Reference Salinity S_R can be obtained from the present function, **gsw_SR_from_SP**, which simply calculates Reference Salinity according to (see section 2.4 and appendix A.3 of IOC *et al*. (2010))

$$S_R \;=\; \frac{35.165\,04\ \mathrm{g\,kg^{-1}}}{35}\ S_P\,. \tag{1}$$

Reference Salinity S_R is the best estimate of the Absolute Salinity of a Standard Seawater sample.

References

IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp. Available from http://www.TEOS-10.org

Here follows sections 2.4 and appendices A.3 of the TEOS-10 Manual (IOC *et al*. (2010)).

2.4 Reference Composition and the Reference-Composition Salinity Scale

The reference composition of seawater is defined by Millero *et al.* (2008a) as the exact mole fractions given in Table D.3 of appendix D below. This composition was introduced by Millero *et al.* (2008a) as their best estimate of the composition of Standard Seawater, being seawater from the surface waters of a certain region of the North Atlantic. The exact location for the collection of bulk material for the preparation of Standard Seawater is not specified. Ships gathering this bulk material are given guidance notes by the Standard Seawater Service, requesting that water be gathered between longitudes 50°W and 40°W, in deep water, during daylight hours. Reference-Composition Salinity S_R (or Reference Salinity for short) was designed by Millero *et al.* (2008b) to be the best estimate of the mass-fraction Absolute Salinity S_A of Standard Seawater. Independent of accuracy considerations, it provides a precise measure of dissolved material in Standard Seawater and is the correct salinity argument to be used in the TEOS-10 Gibbs function for Standard Seawater.

For the range of salinities where Practical Salinities are defined (that is, in the range $2 < S_P < 42$) Millero *et al.* (2008a) show that

$$S_R \approx u_{PS} \, S_P \qquad \text{where} \qquad u_{PS} \equiv (35.165\,04/35)\ \text{g kg}^{-1}. \qquad (2.4.1)$$

In the range $2 < S_P < 42$, this equation expresses the Reference Salinity of a seawater sample on the Reference-Composition Salinity Scale (Millero *et al.* (2008a)). For practical purposes, this relationship can be taken to be an equality since the approximate nature of this relation only reflects the extent to which Practical Salinity, as determined from measurements of conductivity ratio, temperature and pressure, varies when a seawater sample is heated, cooled or subjected to a change in pressure but without exchange of mass with its surroundings. The Practical Salinity Scale of 1978 was designed to satisfy this property as accurately as possible within the constraints of the polynomial approximations used to determine Chlorinity (and hence Practical Salinity) in terms of the measured conductivity ratio.

From Eqn. (2.4.1), a seawater sample of Reference Composition whose Practical Salinity S_P is 35 has a Reference Salinity S_R of 35.165 04 g kg^{-1}. Millero *et al.* (2008a) estimate that the absolute uncertainty in this value is $\pm 0.007\ \text{g kg}^{-1}$. The difference between the numerical values of Reference and Practical Salinities can be traced back to the original practice of determining salinity by evaporation of water from seawater and weighing the remaining solid material. This process also evaporated some volatile components and most of the 0.165 04 g kg^{-1} salinity difference is due to this effect.

Measurements of the composition of Standard Seawater at a Practical Salinity S_P of 35 using mass spectrometry and/or ion chromatography are underway and may provide updated estimates of both the value of the mass fraction of dissolved material in Standard Seawater and its uncertainty. Any update of this value will not change the Reference-Composition Salinity Scale and so will not affect the calculation of Reference Salinity nor of Absolute Salinity as calculated from Reference Salinity plus the Absolute Salinity Anomaly.

Oceanographic databases label stored, processed or exported parameters with the GF3 code PSAL for Practical Salinity and SSAL for salinity measured before 1978 (IOC, 1987). In order to avoid possible confusion in data bases between different types of salinity it is very strongly recommended that under no circumstances should either Reference Salinity or Absolute Salinity be stored in national data bases.

Detailed information on Reference Composition and Reference Salinity can be found in Millero *et al.* (2008a). For the user's convenience a brief summary of information from Millero *et al.* (2008a), including the precise definition of Reference Salinity is given in appendix A.3 and in Table D3 of appendix D.

A.3 Reference Composition and the Reference-Composition Salinity Scale

As mentioned in the main text, the Reference Composition of seawater is defined by Millero *et al.* (2008a) as the exact mole fractions given in Table D.3 of appendix D below. This composition model was determined from the most accurate measurements available of the properties of Standard Seawater, which is filtered seawater from the surface waters of the North Atlantic as made available by the IAPSO Standard Seawater Service. The Reference Composition is perfectly consistent with charge balance of ocean waters and the most recent atomic weight estimates (Wieser (2006)). For seawater with this reference composition the Reference-Composition Salinity S_R as defined below provides our best estimate of the Absolute Salinity.

The Reference Composition includes all important components of seawater having mass fractions greater than about 0.001 g kg^{-1} (i. e. 1.0 mg kg^{-1}) that can significantly affect either the conductivity or the density of seawater having a Practical Salinity of 35. The most significant ions not included are Li$^+$ (~0.18 mg kg^{-1}) and Rb$^+$ (~0.12 mg kg^{-1}). Dissolved gases N_2 (~16 mg kg^{-1}) and O_2 (up to 8 mg kg^{-1} in the ocean) are not included as neither have a significant effect on density or on conductivity. In addition, N_2 remains within a few percent of saturation at the measured temperature in almost all laboratory and in situ conditions. However, the dissolved gas CO_2 (~0.7 mg kg^{-1}), and the ion OH$^-$ (~0.08 mg kg^{-1}) are included in the Reference Composition because of their important role in the equilibrium dynamics of the carbonate system. Changes in pH which involve conversion of CO_2 to and from ionic forms affect conductivity and density. Concentrations of the major nutrients $Si(OH)_4$, NO_3^- and PO_4^{3-} are assumed to be negligible in Standard Seawater; their concentrations in the ocean range from 0-16 mg kg^{-1}, 0-2 mg kg^{-1}, and 0-0.2 mg kg^{-1} respectively. The Reference Composition does not include organic matter. The composition of Dissolved Organic Matter (DOM) is complex and poorly known. DOM is typically present at concentrations of 0.5-2 mg kg^{-1} in the ocean.

Reference-Composition Salinity is defined to be conservative during mixing or evaporation that occurs without removal of sea salt from solution. Because of this property, the Reference-Composition Salinity of any seawater sample can be defined in terms of products determined from the mixture or separation of two precisely defined end members. *Pure water* and *KCl-normalized seawater* are defined for this purpose. Pure water is defined as Vienna Standard Mean Ocean Water, VSMOW, which is described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS (2005), BIPM (2005)); it is taken as the zero reference value. *KCl-normalized seawater* (or normalized seawater for short) is defined to correspond to a seawater sample with a Practical Salinity of 35. Thus, any seawater sample that has the same electrical conductivity as a solution of potassium chloride (KCl) in pure water with the KCl mass fraction of 32.4356 g kg^{-1} when both are at the ITS-90 temperature t = 14.996 °C and one standard atmosphere pressure, P = 101325 Pa is referred to as normalized seawater. Here, KCl refers to the normal isotopic abundances of potassium and chlorine as described by the International Union of Pure and Applied Chemistry (Wieser (2006)). As discussed below, any normalized seawater sample has a Reference-Composition Salinity of 35.165 04 g kg^{-1}.

Since *Reference-Composition Salinity* is defined to be conservative during mixing, if a seawater sample of mass m_1 and Reference-Composition Salinity S_{R1} is mixed with another seawater sample of mass m_2 and Reference-Composition Salinity S_{R2}, the final Reference-Composition Salinity S_{R12} of this sample is

$$S_{R12} = \frac{m_1 S_{R1} + m_2 S_{R2}}{m_1 + m_2} \, . \tag{A.3.1}$$

Negative values of m_1 and m_2, corresponding to the removal of seawater with the appropriate salinity are permitted, so long as $m_1(1 - S_{R1}) + m_2(1 - S_{R2}) > 0$. In particular, if $S_{R2} = 0$ (pure water) and m_2 is the mass of pure water needed to normalize the seawater sample (that is, m_2 is the mass needed to achieve $S_{R12} = 35.165\,04$ g kg^{-1}), then the original Reference-Composition Salinity of sample 1 is given by

$$S_{R1} = [1 + (m_2 / m_1)] \times 35.16504 \ \text{g kg}^{-1}. \tag{A.3.2}$$

The definitions and procedures above allow one to determine the Reference Salinity of any seawater sample at the ITS-90 temperature t = 14.996 °C and one standard atmosphere pressure. To complete the definition, we note that the Reference-Composition Salinity of a seawater sample at given temperature and pressure is equal to the Reference-Composition Salinity of the same sample at any other temperature and pressure provided the transition process is conducted without exchange of matter, in particular, without evaporation, precipitation or degassing of substance from the solution. Note that this property is shared by Practical Salinity to the accuracy of the algorithms used to define this quantity in terms of the conductivity ratio R_{15}.

We noted above that a Practical Salinity of 35 is associated with a Reference Salinity of 35.165 04 g kg^{-1}. This value was determined by Millero *et al.* (2008a) using the reference composition model, the most recent atomic weights (Wieser (2006)) and the relation S = 1.806 55 Cl / (g kg^{-1}) which was used in the original definition of Practical Salinity to convert between measured Chlorinity values and Practical Salinity. Since the relation between Practical Salinity and conductivity ratio was defined using the same conservation relation as satisfied by Reference Salinity, the Reference Salinity can be determined to the same accuracy as Practical Salinity wherever the latter is defined (that is, in the range $2 < S_P < 42$), as

$$S_R \approx u_{PS} S_P \qquad \text{where} \qquad u_{PS} \equiv (35.165\,04/35)\ \text{g kg}^{-1}. \tag{A.3.3}$$

For practical purposes, this relationship can be taken to be an equality since the approximate nature of this relation only reflects the accuracy of the algorithms used in the definition of Practical Salinity. This follows from the fact that the Practical Salinity, like Reference Salinity, is intended to be precisely conservative during mixing and also during changes in temperature and pressure that occur without exchange of mass with the surroundings.

The Reference-Composition Salinity Scale is defined such that a seawater sample whose Practical Salinity S_P is 35 has a Reference-Composition Salinity S_R of precisely 35.165 04 g kg^{-1}. Millero *et al.* (2008a) estimate that the absolute uncertainty associated with using this value as an estimate of the Absolute Salinity of Reference Composition Seawater is ± 0.007 g kg^{-1}. Thus the numerical difference between the Reference Salinity expressed in g kg^{-1} and Practical Salinity is about 24 times larger than this estimate of uncertainty. The difference, 0.165 04, is also large compared to our ability to measure Practical Salinity at sea (which can be as precise as ± 0.002). Understanding how this discrepancy was introduced requires consideration of some historical details that influenced the definition of Practical Salinity. The details are presented in Millero *et al.* (2008a) and in Millero (2010) and are briefly reviewed below.

There are two primary sources of error that contribute to this discrepancy. First, and most significant, in the original evaporation technique used by Sørensen in 1900 (Forch *et al.* 1902) to estimate salinity, some volatile components of the dissolved material were lost so the amount of dissolved material was underestimated. Second, the approximate relation determined by Knudsen (1901) to determine S(‰) from measurements of Cl(‰) was based on analysis of only nine samples (one from the Red Sea, one from the North Atlantic, one from the North Sea and six from the Baltic Sea). Both the errors in estimating absolute Salinity by evaporation and the bias towards Baltic Sea conditions, where strong

composition anomalies relative to North Atlantic conditions are found, are reflected in Knudsen's formula,

$$S_K\left(\text{‰}\right) = 0.03 + 1.805\, Cl\left(\text{‰}\right). \tag{A.3.4}$$

When the Practical Salinity Scale was decided upon in the late 1970s it was known that this relation included significant errors, but it was decided to maintain numerical consistency with this accepted definition of salinity for typical mid-ocean conditions (Millero (2010)). To achieve this consistency while having salinity directly proportional to Chlorinity, the Joint Panel for Oceanographic Tables and Standards (JPOTS) decided to determine the proportionality constant from Knudsen's formula at S_K = 35 ‰ (Cl = 19.3740 ‰), (Wooster *et al.*, 1969). This resulted in the conversion formula

$$S\left(\text{‰}\right) = 1.80655\, Cl\left(\text{‰}\right) \tag{A.3.5}$$

being used in the definition of the practical salinity scale as if it were an identity, thus introducing errors that have either been overlooked or accepted for the past 30 years. We now break with this tradition in order to define a salinity scale based on a composition model for Standard Seawater that was designed to give a much improved estimate of the mass-fraction salinity for Standard Seawater and for Reference-Composition Seawater. The introduction of this salinity scale provides a more physically meaningful measure of salinity and simplifies the task of systematically incorporating the influence of spatial variations of seawater composition into the procedure for estimating Absolute Salinity.

Finally, we note that to define the Reference-Composition Salinity Scale we have introduced the quantity u_{PS} in Eqn. (A.3.3), defined by $u_{PS} \equiv (35.165\,04/35)\ \text{g kg}^{-1}$. This value was determined by the requirement that the Reference-Composition Salinity gives the best estimate of the mass-fraction Absolute Salinity (that is, the mass-fraction of non-H_2O material) of Reference-Composition Seawater. However, the uncertainty in using S_R to estimate the Absolute Salinity of Reference Composition Seawater is at least 0.007 g kg^{-1} at S = 35 (Millero *et al.* (2008b)). Thus, although u_{PS} is precisely specified in the definition of the Reference-Composition Salinity Scale, it must be noted that using the resulting definition of the Reference Salinity to estimate the Absolute Salinity of Reference Composition Seawater does have a non-zero uncertainty associated with it. This and related issues are discussed further in the next subsection.