

Notes on the function `gsw_osmotic_coefficient_t_exact(SA,t,p)`

This function, `gsw_osmotic_coefficient_t_exact(SA,t,p)` evaluates the osmotic coefficient ϕ of seawater from Eqn. (2.14.1) of the TEOS-10 Manual (IOC *et al.*, 2010), namely

$$\phi = \phi(S_A, t, p) = - \left(g(S_A, t, p) - g(0, t, p) - S_A \left. \frac{\partial g}{\partial S_A} \right|_{T,p} \right) (m_{\text{sw}} R (T_0 + t))^{-1}. \quad (2.14.1)$$

where m_{sw} is the molality of seawater which can be evaluated from the GSW function `gsw_molality_from_SA(SA)` from the definition given by Eqn. (3.40.10) of the TEOS-10 Manual (IOC *et al.* (2010))

$$m_{\text{sw}} = \frac{S_A}{(1 - S_A) M_S}. \quad (3.40.10)$$

Here M_S is the mole-weighted average atomic weight of the elements of sea salt. The paper which defines the Reference-Composition Salinity Scale, Millero *et al.* (2008), derives M_S to be the value

$$M_S = 31.403\ 821\ 8\dots \text{ g mol}^{-1} = 0.031\ 403\ 821\ 8\dots \text{ kg mol}^{-1}, \quad (1)$$

and this value is a fundamental constant of TEOS-10 and can be found by calling `gsw_atomic_weight`. In Eqn. (3.40.10) Absolute Salinity S_A must be in units of kg kg^{-1} which means that M_S must be in units of kg mol^{-1} in this equation. Molality m_{sw} is given by the GSW function `gsw_molality_from_SA(SA)` in units of mol kg^{-1} .

This function `gsw_osmotic_coefficient_t_exact(SA,t,p)` uses the full TEOS-10 Gibbs function $g(S_A, t, p)$ of IOC *et al.* (2010), being the sum of the IAPWS-09 and IAPWS-08 Gibbs functions. The molality m_{sw} tends to zero as Absolute Salinity tends to zero, and this would seem to present a problem for the evaluation of the osmotic coefficient from Eqn. (2.14.1). However the combination of the salty part of the Gibbs function and its salinity derivative in this equation also tends to zero linearly as Absolute Salinity tends to zero. The potential singularity at $S_A = 0 \text{ g kg}^{-1}$ is avoided in this function by carefully collecting all the powers of S_A in Eqn. (2.14.1) and mathematically cancelling the leading power of Absolute Salinity. Because of this, `gsw_osmotic_coefficient_t_exact(SA,t,p)` is well-behaved at $S_A = 0 \text{ g kg}^{-1}$ where in fact the value 1.0 is returned.

Strictly speaking, Eqn. (2.14.1) applies only to seawater of Reference Composition because the value of M_S used in this equation is the value for Reference-Composition seawater. The value of the mole-weighted average atomic weight of the elements of seawater of arbitrary composition is unknown. If the osmotic coefficient of seawater of general composition is required to an accuracy of better than 0.1% it is suggested that you contact the authors for further guidance.

References

- IAPWS, 2008: Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater. The International Association for the Properties of Water and Steam. Berlin, Germany, September 2008, available from www.iapws.org. This Release is referred to in the text as **IAPWS-08**.
- IAPWS, 2009: Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use. The International Association for the Properties of Water and Steam. Doorwerth, The Netherlands, September 2009, available from <http://www.iapws.org>. This Release is referred to in the text as **IAPWS-09**.
- 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 section 2.14 of the TEOS-10 Manual (IOC *et al.*, 2010)).

2.14 Osmotic coefficient

The osmotic coefficient of seawater ϕ is given by

$$\phi = \phi(S_A, t, p) = - \left(g(S_A, t, p) - g(0, t, p) - S_A \left. \frac{\partial g}{\partial S_A} \right|_{T, p} \right) (m_{\text{SW}} R (T_0 + t))^{-1}. \quad (2.14.1)$$

The osmotic coefficient of seawater describes the change of the chemical potential of water per mole of added salt, expressed as multiples of the thermal energy, $R(T_0 + t)$ (Millero and Leung (1976), Feistel and Marion (2007), Feistel (2008)),

$$\mu^{\text{W}}(0, t, p) = \mu^{\text{W}}(S_A, t, p) + m_{\text{SW}} R (T_0 + t) \phi. \quad (2.14.2)$$

Here, $R = 8.314\,472 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal molar gas constant. The molality m_{SW} is the number of dissolved moles of solutes (ions) of the Reference Composition as defined by Millero *et al.* (2008a), per kilogram of pure water. Note that the molality of seawater may take different values if neutral molecules of salt rather than ions are counted (see the discussion on page 519 of Feistel and Marion (2007)). The freezing-point lowering equations (3.33.1, 3.33.2) or the vapour-pressure lowering can be computed from the osmotic coefficient of seawater (see Millero and Leung (1976), Bromley *et al.* (1974)).