

**Notes on the function,
gsw_CT_freezing_poly(SA,p,saturation_fraction),
which evaluates the Conservative Temperature at which seawater freezes**

This function, **gsw_CT_freezing_poly**, finds the Conservative Temperature (ITS-90 °C) at which seawater of Absolute Salinity S_A (in g kg^{-1}) freezes at pressure p (dbar). The third argument is optional and is the saturation fraction (between 0 and 1) of the dissolved air in seawater. If this third argument is missing, the seawater is taken to be air free (i. e. saturation_fraction is put equal to 0).

This function is a polynomial fit to the TEOS-10 freezing temperature over the range in $S_A - p$ space between 0 g kg^{-1} and 120 g kg^{-1} and between 0 dbar and 10,000 dbar (100 MPa). There is a triangle of data in $S_A - p$ space at the largest pressures and Absolute Salinities (see below) where TEOS-10 does not provide the freezing temperature, and neither does this **gsw_CT_freezing_poly** function return an answer in this triangle. We have chosen to do the polynomial fit for the Conservative Temperature at which seawater freezes rather than the *in situ* freezing temperature because ocean models will have Conservative Temperature as their temperature variable. The *in situ* temperature at which seawater freezes can be found by first using the present function, **gsw_CT_freezing_poly**, and then calling the function **gsw_t_from_CT**. These two function calls can be performed together by simply calling the GSW function **gsw_t_freezing_poly** (SA,p,saturation_fraction).

The *in situ* freezing temperature is the temperature t_f at which the chemical potential of water in seawater μ^w equals the chemical potential of ice μ^{lh} , and t_f is found by solving Eqn. (3.33.2) of the TEOS-10 Manual (IOC *et al.* (2010), see below). The *in-situ* freezing temperature can be found by this exact method using the function **gsw_t_freezing**(SA,p,saturation_fraction). The TEOS-10 Gibbs function for seawater is valid in the ranges $0 \text{ g kg}^{-1} \leq S_A \leq 42 \text{ g kg}^{-1}$ and $0 \text{ dbar} \leq p \leq 10,000 \text{ dbar}$. Additionally, at $p = 0 \text{ dbar}$ TEOS-10 is valid for Absolute Salinity up to where a constituent of seawater first saturates and come out of solution. This typically occurs at an Absolute Salinity of between 90 g kg^{-1} and 110 g kg^{-1} (Feistel and Marion (2007), Marion *et al.* (2009)). Technically we should restrict the range of applicability of our polynomial fit to this area of $S_A - p$ space plus the line at $p = 0 \text{ dbar}$ up to the Absolute Salinity of saturation, but the work of Feistel and Marion (2007) (see their figure 15) suggests that the freezing temperatures calculated using the TEOS-10 Gibbs function at high pressures beyond $S_A = 42 \text{ g kg}^{-1}$ will not contain gross errors.

In the region of validity of the TEOS-10 Gibbs function, the r.m.s. accuracy of the freezing temperature is estimated to be 1.5mK (see section 6.3, figure 4 and table 7 of Feistel (2008)). The polynomial of **gsw_CT_freezing_poly** fits the full TEOS-10 Θ freezing temperature to within $\pm 0.6\text{mK}$ over both the valid TEOS-10 $S_A - p$ range and the extrapolated region. Hence we conclude that the use of **gsw_CT_freezing_poly** is essentially as accurate as the full TEOS-10 approach for calculating the freezing temperature. The SIA code of TEOS-10 from which we obtained the freezing temperatures that underlie this fit returns values for the freezing temperature down to about -12°C . This *in situ* freezing temperature corresponds approximately to the line in (S_A, p) space connecting $(50 \text{ g kg}^{-1}, 10\,000 \text{ dbar})$ to $(120 \text{ g kg}^{-1}, 5\,000 \text{ dbar})$, and **gsw_CT_freezing_poly** and **gsw_t_freezing_poly** return Nans if the input Absolute Salinity and pressure lie beyond this line in $S_A - p$ space.

The polynomial of this **gsw_CT_freezing_poly** function, for air-free seawater, is

$$\left(\frac{\text{CT}^{\text{freeze}}}{^{\circ}\text{C}} \right) = c_{00} + \sum_{j=2}^7 \sum_{k=0}^3 c_{jk} \left(\frac{S_A}{100 \text{ g kg}^{-1}} \right)^{j/2} \left(\frac{p}{10000 \text{ dbar}} \right)^k \quad \text{air-free seawater} \quad (1)$$

where the coefficients $c_{j,k}$ are

$$\begin{aligned} c_{00} &= 0.017947064327968736; \\ c_{20} &= -6.076099099929818; \\ c_{30} &= 4.883198653547851; \\ c_{40} &= -11.88081601230542; \\ c_{50} &= 13.34658511480257; \\ c_{60} &= -8.722761043208607; \\ c_{70} &= 2.082038908808201; \\ c_{01} &= -7.389420998107497; \\ c_{21} &= -0.9891538123307282; \\ c_{31} &= -0.08987150128406496; \\ c_{41} &= 1.054318231187074; \\ c_{51} &= 0.3850133554097069; \\ c_{61} &= -2.079022768390933; \\ c_{71} &= 1.242891021876471; \\ c_{02} &= -2.110913185058476; \\ c_{22} &= 0.3831132432071728; \\ c_{32} &= 1.065556599652796; \\ c_{42} &= -2.078616693017569; \\ c_{52} &= 1.596435439942262; \\ c_{03} &= 0.2295491578006229; \\ c_{23} &= -0.7997496801694032; \\ c_{33} &= 0.8756340772729538; \\ c_{43} &= 0.1338002171109174; \end{aligned}$$

Note that there are no coefficients with $j = 1$, as the square root of Absolute Salinity does not appear in the TEOS-10 polynomial for the chemical potential of water in seawater, μ^{W} . The *in situ* freezing temperature t_f of air-free pure water at $p = 0$ dbar is known very accurately (with an uncertainty of only $2 \mu\text{K}$) to be $0.002519 \text{ } ^{\circ}\text{C}$. In terms of Conservative Temperature Θ this is $0.017947064327968736 \text{ } ^{\circ}\text{C}$ (since **gsw_CT_from_pt**(0,0.002519) = $0.017947064327968736 \text{ } ^{\circ}\text{C}$), and this is the value of c_{00} above.

The presence of dissolved air in seawater

If there is dissolved air in seawater, the freezing temperature is lowered. The depression of the *in situ* freezing temperature of pure water (i.e. $S_A = 0 \text{ g kg}^{-1}$) at $p = 0$ dbar is 2.4 mK, while for Standard Seawater with $S_A = 35.16504 \text{ g kg}^{-1}$ the *in situ* freezing temperature depression is 1.9 mK. The variation of the θ freezing point depression is normally taken to be a linear function of salinity (section 6.3 of Feistel (2008)).

The rate at which Conservative Temperature changes with potential temperature at fixed Absolute Salinity $\tilde{\Theta}_\theta$ is given by (see Eqn. (A.12.3a) of the TEOS-10 manual (IOC *et al.* (2010)))

$$\tilde{\Theta}_\theta = \left. \frac{\partial \Theta}{\partial \theta} \right|_{S_A} = \frac{c_p(S_A, \theta, 0)}{c_p^0}, \quad (2)$$

showing that $\tilde{\Theta}_\theta$ is proportional to the specific heat of seawater at $p = 0$ dbar, and we note that $c_p(S_A, \theta, 0)$ is approximately a linear function of Absolute Salinity (see Figure 4 of the TEOS-10 manual). We use this approximate linear variation of $\tilde{\Theta}_\theta$ with S_A to motivate the Θ freezing temperature depression in terms of the θ freezing temperature depression, obtaining the following final expression for the Θ freezing temperature,

$$\left(\frac{\text{CT}^{\text{freeze}}}{^\circ\text{C}} \right) = c_{00} + \sum_{j=2}^7 \sum_{k=0}^3 c_{jk} \left(\frac{S_A}{100 \text{ g kg}^{-1}} \right)^{j/2} \left(\frac{p}{10000 \text{ dbar}} \right)^k - (\text{saturation_fraction}) \left(2.4 - a \frac{S_A}{(35.16504 \text{ g kg}^{-1})} \right) \left(1 + b \left[1 - \frac{S_A}{(35.16504 \text{ g kg}^{-1})} \right] \right) 10^{-3}, \quad (3)$$

with $a = 0.502500117621$ and $b = 0.057000649899720$. These two coefficients have been chosen so that the *in situ* temperature freezing point depression for air-saturated seawater at $p = 0$ dbar is exactly 2.4 mK at $S_A = 0 \text{ g kg}^{-1}$ and exactly 1.9 mK at $S_A = 35.16504 \text{ g kg}^{-1}$.

References

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- Marion, G. M., F. J. Millero, and R. Feistel, 2009: Precipitation of solid phase calcium carbonates and their effect on application of seawater $S_A - T - P$ models, *Ocean Sci.*, **5**, 285-291. <http://www.ocean-sci.net/5/285/2009/os-5-285-2009.pdf>
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Here follows sections 3.33, 3.34 and 3.42 of the TEOS-10 Manual (IOC *et al.* (2010)).

3.33 Freezing temperature

Freezing occurs at the temperature t_f at which the chemical potential of water in seawater μ^W equals the chemical potential of ice μ^{lh} . Thus, t_f is found by solving the implicit equation

$$\mu^W(S_A, t_f, p) = \mu^{lh}(t_f, p) \quad (3.33.1)$$

or equivalently, in terms of the two Gibbs functions,

$$g(S_A, t_f, p) - S_A g_{S_A}(S_A, t_f, p) = g^{lh}(t_f, p). \quad (3.33.2)$$

The Gibbs function for ice Ih, $g^{lh}(t, p)$, is defined by IAPWS-06 (IAPWS (2009a)) and Feistel and Wagner (2006) and is summarized in appendix I below. In the special case of zero salinity, the chemical potential of water in seawater reduces to the Gibbs function of pure water, $\mu^W(0, t, p) = g^W(t, p)$. A simple correlation function for the melting pressure as a function of temperature is available from IAPWS (2008b) and has been implemented in the SIA library.

At the ocean surface, $p = 0$ dbar, from Eqn. (3.33.1) the TEOS-10 freezing point of pure water is $t_f(0 \text{ g kg}^{-1}, 0 \text{ dbar}) = 0.002 519 \text{ }^\circ\text{C}$ with an uncertainty of only $2 \text{ } \mu\text{K}$, noting that the triple point temperature of water is exactly 273.16 K by definition of the ITS-90 temperature scale. The freezing temperature of the standard ocean is $t_f(S_{SO}, 0 \text{ dbar}) = -1.919 \text{ }^\circ\text{C}$ with an uncertainty of 2 mK . Note that Eqn. (3.33.1) is valid for air-free water/seawater. Dissolution of air in water lowers the freezing point slightly; saturation with air lowers the freezing temperatures by about 2 mK .

To estimate the effects of small changes in the pressure or salinity on the freezing temperature, it is convenient to consider a power series expansion of (3.33.1). The result in the limit of an infinitesimal pressure change at fixed salinity gives the pressure coefficient of freezing point lowering, as (Clausius-Clapeyron equation, Feistel *et al.* (2010a)),

$$\left. \frac{\partial t_f}{\partial p} \right|_{S_A} = \chi_p(S_A, p) = - \frac{g_p - S_A g_{S_A p} - g_p^{lh}}{g_T - S_A g_{S_A T} - g_T^{lh}}. \quad (3.33.3)$$

Its values, evaluated from TEOS-10, vary only weakly with salinity between $\chi_p(0 \text{ g kg}^{-1}, 0 \text{ dbar}) = -0.7429 \text{ mK/dbar}$ for pure water and $\chi_p(S_{SO}, 0 \text{ dbar}) = -0.7483 \text{ mK/dbar}$ for the standard ocean. TEOS-10 is consistent with the most accurate measurement of χ_p and its experimental uncertainty of 0.0015 mK/dbar (Feistel and Wagner (2005), (2006)). Since the value of $|\chi_p|$ always exceeds that of the adiabatic lapse rate $|\Gamma|$, cold seawater may freeze and decompose into ice and brine during adiabatic uplift but this can never happen to a sinking parcel.

In the limit of infinitesimal changes in Absolute Salinity at fixed pressure, we obtain the saline coefficient of freezing point lowering, as (Raoult's law),

$$\left. \frac{\partial t_f}{\partial S_A} \right|_p = \chi_S(S_A, p) = \frac{S_A g_{S_A S_A}}{g_T - S_A g_{S_A T} - g_T^{lh}}. \quad (3.33.4)$$

Typical numerical values are $\chi_S(0 \text{ g kg}^{-1}, 0 \text{ dbar}) = -59.2 \text{ mK}/(\text{g kg}^{-1})$ for pure water and $\chi_S(S_{SO}, 0 \text{ dbar}) = -56.9 \text{ mK}/(\text{g kg}^{-1})$ for seawater.

As a raw practical estimate, Eqn. (3.33.4) can be expanded into powers of salinity, using only the leading term of the TEOS-10 saline Gibbs function, $g^S \approx R_S T S_A \ln S_A$, which stems from Planck's ideal-solution theory (Planck (1888)). Here, $R_S = R/M_S = 264.7599 \text{ J kg}^{-1} \text{ K}^{-1}$ is the specific gas constant of sea salt, R is the universal molar gas constant, and $M_S = 31.403 82 \text{ g mol}^{-1}$ is the molar mass of sea salt with Reference Composition. The denominator of Eqn. (3.33.4) is proportional to the melting heat L_p^{SI} , Eqn. (3.34.7). The convenient result obtained with these simplifications is

$$\left. \frac{\partial t_f}{\partial S_A} \right|_p \approx -\frac{R_S}{L_p^{SI}}(T_0 + t_f)^2 \approx -59 \text{ mK}/(\text{g kg}^{-1}). \quad (3.33.5)$$

where we have used $t_f = -2^\circ\text{C}$ and $L_p^{SI} = 330 \text{ J kg}^{-1}$ as approximations that are appropriate for the standard ocean. This simple result is only weakly dependent on these choices and is in reasonable agreement with the exact values from Eqn. (3.33.4) and with Millero and Leung (1976). The freezing temperature of seawater is always lower than that of pure water.

When sea-ice is formed, it often contains remnants of seawater included in brine pockets. At equilibrium, the salinity in these pockets depends only on temperature and pressure, rather than, for example, on the pocket volume, and can be computed in the functional form $S_A(t, p)$ as an implicit solution of Eqn. (3.33.1). Measured values for the brine salinity of Antarctic sea ice agree very well with those computed of Eqn. (3.33.1) up to the saturation concentration of about 110 g kg^{-1} at surface pressure (Feistel *et al.* (2010b)). At high pressures, the validity of the Gibbs function of seawater, and therefore of the computed freezing point or brine salinity, too, is limited to only 50 g kg^{-1} .

We note that in the first approximation, as inferred from Planck's theory of ideal solutions, the above properties depend on the number of dissolved particles regardless of the particle sizes, masses or charges. In other words, they depend mainly on the molar rather than on the mass density of the solute, in contrast to properties such as the density of seawater and properties derived from it. The properties considered in the remainder of this section (3.33-3.42) which share this attribute are referred to as the colligative properties of seawater.

3.34 Latent heat of melting

The melting process of ice in pure water can be conducted by supplying heat at constant pressure. If this is done slowly enough that equilibrium is maintained, then the temperature will also remain constant. The heat required per mass of molten ice is the latent heat, or enthalpy, of melting, L_p^{WI} . It is found as the difference between the specific enthalpy of water, h^W , and the specific enthalpy of ice, h^{lh} , (Kirchhoff's law, Curry and Webster (1999)):

$$L_p^{WI}(p) = h^W(t_f, p) - h^{lh}(t_f, p). \quad (3.34.1)$$

Here, $t_f(p)$ is the freezing temperature of water, section 3.33. The enthalpies h^W and h^{lh} are available from IAPWS-95 (IAPWS (2009b)) and IAPWS-06 (IAPWS (2009a)), respectively.

In the case of seawater, the melt water will additionally mix with the ambient brine, thus changing the salinity and the freezing temperature of the seawater. Consequently, the enthalpy related to this phase transition will depend on the particular conditions under which the melting occurs.

Here, we define the latent heat of melting as the enthalpy increase per infinitesimal mass of molten ice of a composite system consisting of ice and seawater, when the temperature is increased at constant pressure and at constant total masses of water and salt, in excess to the heat needed to warm up the seawater and ice phases individually (Feistel and Hagen (1998), Feistel *et al.* (2010b)). Mass conservation of both water and salt during this thermodynamic process is essential to ensure the independence of the latent heat formula from the unknown absolute enthalpies of salt and water that otherwise would accompany any mass exchange.

The enthalpy of sea ice, h^{SI} , is additive with respect to its constituents ice, h^{lh} , with the mass fraction w^{lh} , and seawater, h , with the liquid mass fraction $(1 - w^{lh})$:

$$h^{\text{SI}} = (1 - w^{\text{lh}})h(S_{\text{A}}, t, p) + w^{\text{lh}}h^{\text{lh}}(t, p). \quad (3.34.2)$$

Upon warming, the mass of melt water changes the ice fraction w^{lh} and the brine salinity S_{A} . The related temperature derivative of Eqn. (3.34.2) is

$$\left. \frac{\partial h^{\text{SI}}}{\partial T} \right|_p = (1 - w^{\text{lh}}) \left. \frac{\partial h}{\partial T} \right|_{S_{\text{A}}, p} + (1 - w^{\text{lh}}) \left. \frac{\partial h}{\partial S_{\text{A}}} \right|_{T, p} \left. \frac{\partial S_{\text{A}}}{\partial T} \right|_p + w^{\text{lh}} \left. \frac{\partial h^{\text{lh}}}{\partial T} \right|_p + (h^{\text{lh}} - h) \left. \frac{\partial w^{\text{lh}}}{\partial T} \right|_p. \quad (3.34.3)$$

The rate of brine salinity change with temperature is given by the reciprocal of Eqn. (3.33.4) and is related to the isobaric melting rate, $-\partial w^{\text{lh}} / \partial T|_p$, by the conservation of the total salt, $(1 - w^{\text{lh}})S_{\text{A}} = \text{const}$, in the form

$$\left. \frac{\partial S_{\text{A}}}{\partial T} \right|_p = \frac{S_{\text{A}}}{1 - w^{\text{lh}}} \left. \frac{\partial w^{\text{lh}}}{\partial T} \right|_p. \quad (3.34.4)$$

Using this relation, Eqn. (3.34.3) takes the simplified form

$$\left. \frac{\partial h^{\text{SI}}}{\partial T} \right|_p = (1 - w^{\text{lh}})c_p + w^{\text{lh}}c_p^{\text{lh}} - L_p^{\text{SI}} \left. \frac{\partial w^{\text{lh}}}{\partial T} \right|_p. \quad (3.34.5)$$

The coefficient in front of the melting rate,

$$L_p^{\text{SI}}(S_{\text{A}}, p) = h - S_{\text{A}} \left. \frac{\partial h}{\partial S_{\text{A}}} \right|_{T, p} - h^{\text{lh}}, \quad (3.34.6)$$

provides the desired expression for isobaric melting enthalpy, namely the difference between the partial specific enthalpies of water in seawater and of ice. As is physically required for any measurable thermodynamic quantity, the arbitrary absolute enthalpies of ice, water and salt cancel in the formula (3.34.6), provided that the reference state conditions for the ice and seawater formulations are chosen consistently (Feistel *et al.* (2008a)). Note that because of $h = g + (T_0 + t)\eta$ and Eqn. (3.33.2), the latent heat can also be written in terms of entropies η rather than enthalpies h , in the form

$$L_p^{\text{SI}}(S_{\text{A}}, p) = (T_0 + t_f) \times \left(\eta - S_{\text{A}} \left. \frac{\partial \eta}{\partial S_{\text{A}}} \right|_{T, p} - \eta^{\text{lh}} \right). \quad (3.34.7)$$

Again the result is independent of unknown (and unknowable) constants.

The latent heat of melting depends only weakly on salinity and on pressure. At the surface pressure, the computed value is $L_p^{\text{SI}}(0, 0) = L_p^{\text{WI}}(0) = 333\,426.5 \text{ J kg}^{-1}$ for pure water, and $L_p^{\text{SI}}(S_{\text{SO}}, 0) = 329\,928.5 \text{ J kg}^{-1}$ for the standard ocean, with a difference of about 1% due to the dissolved salt. At a pressure of 1000 dbar, these values reduce by 0.6% to $L_p^{\text{SI}}(0, 1000 \text{ dbar}) = L_p^{\text{WI}}(1000 \text{ dbar}) = 331\,528 \text{ J kg}^{-1}$ and $L_p^{\text{SI}}(S_{\text{SO}}, 1000 \text{ dbar}) = 328\,034 \text{ J kg}^{-1}$. TEOS-10 is consistent with the most accurate measurements of L_p^{WI} and their experimental uncertainties of 200 J kg^{-1} , or 0.06% (Feistel and Wagner (2005), (2006)).

Note that in this section 3.42 of the TEOS-10 Manual (IOC *et al.* (2010)) below, some *in situ* freezing temperatures of air-free seawater are listed.

3.42 Temperature of maximum density

At about 4 °C and atmospheric pressure, pure water has a density maximum below which the thermal expansion coefficient and the adiabatic lapse rate change their signs (Röntgen (1892), McDougall and Feistel (2003)). At salinities higher than 23.8 g kg⁻¹ the temperature of maximum density t_{MD} is below the freezing point t_f (Table 3.42.1). The seasonal and spatial interplay between density maximum and freezing point is highly important for the stratification stability and the seasonal deep convection for brackish estuaries with permanent vertical and lateral salinity gradients such as the Baltic Sea (Feistel *et al.* (2008b), Leppäranta and Myrberg (2009), Reissmann *et al.* (2009)).

The temperature of maximum density t_{MD} is computed from the condition of vanishing thermal expansion coefficient, that is, from the solution of the implicit equation for $t_{MD}(S_A, p)$,

$$g_{TP}(S_A, t_{MD}, p) = 0. \quad (3.42.1)$$

The temperature of maximum density is available in the GSW Oceanographic Toolbox as function `gsw_t_maxdensity_exact`. Selected TEOS-10 values computed from Eqn. (3.42.1) are given in Table 3.42.1.

Table 3.42.1: Freezing temperature t_f and temperature of maximum density t_{MD} for air-free brackish seawater with absolute salinities S_A between 0 and 25 g kg⁻¹, computed at the surface pressure from TEOS-10. Values of t_{MD} in parentheses are less than the freezing temperature.

S_A g kg ⁻¹	t_f °C	t_{MD} °C	S_A g kg ⁻¹	t_f °C	t_{MD} °C	S_A g kg ⁻¹	t_f °C	t_{MD} °C
0	+0.003	3.978	8.5	-0.456	2.128	17	-0.912	0.250
0.5	-0.026	3.868	9	-0.483	2.019	17.5	-0.939	0.139
1	-0.054	3.758	9.5	-0.509	1.909	18	-0.966	0.027
1.5	-0.081	3.649	10	-0.536	1.800	18.5	-0.994	-0.085
2	-0.108	3.541	10.5	-0.563	1.690	19	-1.021	-0.196
2.5	-0.135	3.432	11	-0.590	1.580	19.5	-1.048	-0.308
3	-0.162	3.324	11.5	-0.616	1.470	20	-1.075	-0.420
3.5	-0.189	3.215	12	-0.643	1.360	20.5	-1.102	-0.532
4	-0.216	3.107	12.5	-0.670	1.249	21	-1.130	-0.644
4.5	-0.243	2.999	13	-0.697	1.139	21.5	-1.157	-0.756
5	-0.269	2.890	13.5	-0.724	1.028	22	-1.184	-0.868
5.5	-0.296	2.782	14	-0.750	0.917	22.5	-1.212	-0.980
6	-0.323	2.673	14.5	-0.777	0.807	23	-1.239	-1.092
6.5	-0.349	2.564	15	-0.804	0.696	23.5	-1.267	-1.204
7	-0.376	2.456	15.5	-0.831	0.584	24	-1.294	(-1.316)
7.5	-0.403	2.347	16	-0.858	0.473	24.5	-1.322	(-1.428)
8	-0.429	2.238	16.5	-0.885	0.362	25	-1.349	(-1.540)