

Notes on the function gsw_enthalpy_first_derivatives_CT_exact(SA,CT,p)

This function, **gsw_enthalpy_first_derivatives_CT_exact**(SA,CT,p), evaluates two of the first order partial derivatives of enthalpy $h = \hat{h}(S_A, \Theta, p)$, namely the ones with respect to Absolute Salinity and Conservative Temperature. These derivatives were derived by McDougall (2003), and are given in Eqns. (A.11.15) and (A.11.18) of the TEOS-10 Manual (IOC *et al.*, 2010), repeated here.

$$\hat{h}_\Theta = \frac{(T_0 + t)}{(T_0 + \theta)} c_p^0, \quad (\text{A.11.15})$$

and

$$\hat{h}_{S_A} = g_{S_A}(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} g_{S_A}(S_A, \theta, 0). \quad (\text{A.11.18})$$

This function 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 function first calculates both in situ temperature t and potential temperature θ . From these variables, \hat{h}_Θ is readily calculated, as is the specific volume $v(S_A, t, p)$ and hence \hat{h}_p . Both the terms $g_{S_A}(S_A, \theta, 0)$ and $g_{S_A}(S_A, t, p)$ on the right-hand side of Eqn. (A.11.18) contain logarithmic singularities in the square root of Absolute Salinity, but these singularities exactly cancel in Eqn. (A.11.18). Hence, in the **gsw_enthalpy_first_derivatives_CT_exact**(SA,CT,p) code the right-hand side of Eqn. (A.11.18) is not simply calculated by twice calling the S_A derivative of the Gibbs function, but rather, the polynomials representing both $g_{S_A}(S_A, \theta, 0)$ and $g_{S_A}(S_A, t, p)$ are incorporated into the code, and the logarithm terms are deliberately excluded. In this way, this function can be used with the input value of S_A being exactly zero. All three first derivatives are well behaved as Absolute Salinity approaches zero, as well as at $S_A = 0 \text{ g kg}^{-1}$.

The pressure derivative of enthalpy $h_p|_{S_A, \Theta}$ is not returned from this function as it is specific volume v which can be evaluated by calling **gsw_specvol_CT_exact**(SA,CT,p).

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>
- McDougall, T. J., 2003: Potential enthalpy: A conservative oceanic variable for evaluating heat content and heat fluxes. *Journal of Physical Oceanography*, **33**, 945-963.

Here follows appendices A.10, A.11 and A.12 of the TEOS-10 Manual (IOC *et al.*, 2010).

A.10 Proof that $\theta = \theta(S_A, \eta)$ and $\Theta = \Theta(S_A, \theta)$

Consider changes occurring at the sea surface, (specifically at $p = 0$ dbar) where the temperature is the same as the potential temperature referenced to 0 dbar and the increment of pressure dp is zero. Regarding specific enthalpy h and chemical potential μ to be functions of entropy η (in place of temperature t), that is, considering the functional form of h and μ to be $h = \hat{h}(S_A, \eta, p)$ and $\mu = \hat{\mu}(S_A, \eta, p)$, it follows from the fundamental thermodynamic relation (Eqn. (A.7.1)) that

$$\hat{h}_\eta(S_A, \eta, 0) d\eta + \hat{h}_{S_A}(S_A, \eta, 0) dS_A = (T_0 + \theta) d\eta + \hat{\mu}(S_A, \eta, 0) dS_A, \quad (\text{A.10.1})$$

which shows that specific entropy η is simply a function of Absolute Salinity S_A and potential temperature θ , that is $\eta = \eta(S_A, \theta)$, with no separate dependence on pressure. It follows that $\theta = \theta(S_A, \eta)$.

Similarly, from the definition of potential enthalpy and Conservative Temperature in Eqns. (3.2.1) and (3.3.1), at $p = 0$ dbar it can be seen that the fundamental thermodynamic relation (A.7.1) implies

$$c_p^0 d\Theta = (T_0 + \theta) d\eta + \tilde{\mu}(S_A, \theta, 0) dS_A. \quad (\text{A.10.2})$$

This shows that Conservative Temperature is also simply a function of Absolute Salinity and potential temperature, $\Theta = \Theta(S_A, \theta)$, with no separate dependence on pressure. It then follows that Θ may also be expressed as a function of only S_A and η . It follows that Θ has the “potential” property.

A.11 Various isobaric derivatives of specific enthalpy

Because of the central role of enthalpy in the transport and the conservation of “heat” in the ocean, the derivatives of specific enthalpy at constant pressure are here derived with respect to Absolute Salinity and with respect to the three “temperature-like” variables η , θ and Θ as well as *in situ* temperature t .

We begin by noting that the three standard derivatives of $h = h(S_A, t, p)$ when *in situ* temperature t is taken as the “temperature-like” variable are

$$\partial h / \partial S_A|_{T,p} = \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, t, p), \quad (\text{A.11.1})$$

$$\partial h / \partial T|_{S_A,p} = c_p(S_A, t, p) = (T_0 + t) \eta_T(S_A, t, p), \quad (\text{A.11.2})$$

$$\partial h / \partial P|_{S_A,T} = v(S_A, t, p) - (T_0 + t) v_T(S_A, t, p). \quad (\text{A.11.3})$$

Now considering specific enthalpy to be a function of entropy (rather than of temperature t), that is, taking $h = \hat{h}(S_A, \eta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\hat{h}_\eta d\eta + \hat{h}_{S_A} dS_A = (T_0 + t) d\eta + \mu dS_A \quad \text{while} \quad \partial \hat{h} / \partial P|_{S_A, \eta} = v, \quad (\text{A.11.4})$$

so that

$$\partial \hat{h} / \partial \eta|_{S_A,p} = (T_0 + t) \quad \text{and} \quad \partial \hat{h} / \partial S_A|_{\eta,p} = \mu. \quad (\text{A.11.5})$$

Now taking specific enthalpy to be a function of potential temperature (rather than of temperature t), that is, taking $h = \tilde{h}(S_A, \theta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\tilde{h}_\theta d\theta + \tilde{h}_{S_A} dS_A = (T_0 + t) d\eta + \mu dS_A \quad \text{while} \quad \partial \tilde{h} / \partial P|_{S_A, \theta} = v. \quad (\text{A.11.6})$$

To evaluate the \tilde{h}_θ partial derivative, it is first written in terms of the derivative with respect to entropy as

$$\tilde{h}_\theta|_{S_A, p} = \eta_\theta|_{S_A} \tilde{h}_\eta|_{S_A, p} = \eta_\theta|_{S_A} (T_0 + t), \quad (\text{A.11.7})$$

where (A.11.5) has been used. This equation can be evaluated at $p = 0$ when it becomes (the potential temperature used here is referenced to $p_r = 0$)

$$\tilde{h}_\theta|_{S_A, p=0} = c_p(S_A, \theta, 0) = \eta_\theta|_{S_A} (T_0 + \theta). \quad (\text{A.11.8})$$

These two equations are used to arrive at the desired expression for \tilde{h}_θ namely

$$\tilde{h}_\theta|_{S_A, p} = c_p(S_A, \theta, 0) \frac{(T_0 + t)}{(T_0 + \theta)} = -(T_0 + t) g_{TT}(S_A, \theta, 0). \quad (\text{A.11.9})$$

To evaluate the \tilde{h}_{S_A} partial derivative, we first write specific enthalpy in the functional form $h = \hat{h}(S_A, \eta(S_A, \theta), p)$ and then differentiate it, finding

$$\tilde{h}_{S_A}|_{\theta, p} = \tilde{h}_{S_A}|_{\eta, p} + \tilde{h}_\eta|_{S_A, p} \eta_{S_A}|_\theta. \quad (\text{A.11.10})$$

The partial derivative of specific entropy $\eta = -g_T$ (Eqn. (2.10.1)) with respect to Absolute Salinity, $\eta_{S_A} = -g_{S_A T}$, is also equal to $-\mu_T$ since chemical potential is defined by Eqn. (2.9.6) as $\mu = g_{S_A}$. Since the partial derivative of entropy with respect to S_A in (A.11.10) is performed at fixed potential temperature (rather than at fixed *in situ* temperature), this is equal to $-\mu_T$ evaluated at $p = 0$. Substituting both parts of (A.11.5) into (A.11.10) we have the desired expression for \tilde{h}_{S_A} namely

$$\begin{aligned} \tilde{h}_{S_A}|_{\theta, p} &= \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - (T_0 + t) g_{TS_A}(S_A, \theta, 0). \end{aligned} \quad (\text{A.11.11})$$

Notice that this expression contains some things that are evaluated at the general pressure p and one evaluated at the reference pressure $p_r = 0$.

Now considering specific enthalpy to be a function of Conservative Temperature (rather than of temperature t), that is, taking $h = \hat{h}(S_A, \Theta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\hat{h}_\Theta d\Theta + \hat{h}_{S_A} dS_A = (T_0 + t) d\eta + \mu dS_A \quad \text{while} \quad \partial \hat{h} / \partial P|_{S_A, \Theta} = v. \quad (\text{A.11.12})$$

The partial derivative \hat{h}_Θ follows directly from this equation as

$$\hat{h}_\Theta|_{S_A, p} = (T_0 + t) \eta_\Theta|_{S_A, p} = (T_0 + t) \eta_\Theta|_{S_A}. \quad (\text{A.11.13})$$

At $p = 0$ this equation reduces to

$$\hat{h}_\Theta|_{S_A, p=0} = c_p^0 = (T_0 + \theta) \eta_\Theta|_{S_A}, \quad (\text{A.11.14})$$

and combining these two equations gives the desired expression for \hat{h}_Θ namely

$$\hat{h}_\Theta|_{S_A, p} = \frac{(T_0 + t)}{(T_0 + \theta)} c_p^0. \quad (\text{A.11.15})$$

To evaluate the \hat{h}_{S_A} partial derivative we first write h in the functional form $h = \hat{h}(S_A, \eta(S_A, \Theta), p)$ and then differentiate it, finding (using both parts of Eqn. (A.11.5))

$$\hat{h}_{S_A}|_{\Theta, p} = \mu(S_A, t, p) + (T_0 + t) \eta_{S_A}|_\Theta. \quad (\text{A.11.16})$$

The differential expression Eqn. (A.11.12) can be evaluated at $p = 0$ where the left-hand side is simply $c_p^0 d\Theta$ so that from Eqn. (A.11.12) we find that

$$\eta_{S_A}|_{\Theta} = -\frac{\mu(S_A, \theta, 0)}{(T_0 + \theta)}, \quad (\text{A.11.17})$$

so that the desired expression for \hat{h}_{S_A} is

$$\boxed{\begin{aligned} \hat{h}_{S_A}|_{\Theta, p} &= \mu(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} g_{S_A}(S_A, \theta, 0). \end{aligned}} \quad (\text{A.11.18})$$

The above boxed expressions for four different isobaric derivatives of specific enthalpy are important as they are integral to forming the First Law of Thermodynamics in terms of potential temperature and in terms of Conservative Temperature. The partial derivatives \hat{h}_{Θ} and \hat{h}_{S_A} of Eqns. (A.11.15) and (A.11.18) can be calculated using the GSW Oceanographic Toolbox function **gsw_enthalpy_first_derivatives**.

The second order partial derivatives $\hat{h}_{\Theta\Theta}$, $\hat{h}_{S_A\Theta}$ and $\hat{h}_{S_AS_A}$ can be written in terms of the seawater Gibbs function as (from McDougall *et al.* (2011b))

$$h_{\Theta\Theta}|_{S_A, p} = \hat{h}_{\Theta\Theta} = \frac{(c_p^0)^2}{(T_0 + \theta)^2} \left(\frac{(T_0 + t)}{(T_0 + \theta)} \frac{1}{g_{TT}(S_A, \theta, 0)} - \frac{1}{g_{TT}(S_A, t, p)} \right), \quad (\text{A.11.19})$$

$$\begin{aligned} \hat{h}_{S_A\Theta} &= \frac{c_p^0}{(T_0 + \theta)} \left(\frac{(T_0 + t)}{(T_0 + \theta)} \frac{g_{S_AT}(S_A, \theta, 0)}{g_{TT}(S_A, \theta, 0)} - \frac{g_{S_AT}(S_A, t, p)}{g_{TT}(S_A, t, p)} \right) \\ &\quad - \frac{c_p^0 g_{S_A}(S_A, \theta, 0)}{(T_0 + \theta)^2} \left(\frac{(T_0 + t)}{(T_0 + \theta)} \frac{1}{g_{TT}(S_A, \theta, 0)} - \frac{1}{g_{TT}(S_A, t, p)} \right), \end{aligned} \quad (\text{A.11.20})$$

and

$$\begin{aligned} \hat{h}_{S_AS_A} &= g_{S_AS_A}(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} g_{S_AS_A}(S_A, \theta, 0) \\ &\quad + \frac{(T_0 + t)}{(T_0 + \theta)} \frac{[g_{S_AT}(S_A, \theta, 0)]^2}{g_{TT}(S_A, \theta, 0)} - \frac{[g_{S_AT}(S_A, t, p)]^2}{g_{TT}(S_A, t, p)} \\ &\quad - \frac{2 g_{S_A}(S_A, \theta, 0)}{(T_0 + \theta)} \left(\frac{(T_0 + t)}{(T_0 + \theta)} \frac{g_{S_AT}(S_A, \theta, 0)}{g_{TT}(S_A, \theta, 0)} - \frac{g_{S_AT}(S_A, t, p)}{g_{TT}(S_A, t, p)} \right) \\ &\quad + \frac{[g_{S_A}(S_A, \theta, 0)]^2}{(T_0 + \theta)^2} \left(\frac{(T_0 + t)}{(T_0 + \theta)} \frac{1}{g_{TT}(S_A, \theta, 0)} - \frac{1}{g_{TT}(S_A, t, p)} \right). \end{aligned} \quad (\text{A.11.21})$$

These second order partial derivatives can be calculated using the GSW Oceanographic Toolbox function **gsw_enthalpy_second_derivatives**.

A.12 Differential relationships between η , θ , Θ and S_A

Evaluating the fundamental thermodynamic relation in the forms (A.11.6) and (A.11.12) and using the four boxed equations in appendix A.11, we find the relations

$$\begin{aligned} (T_0+t)d\eta+\mu(p)dS_A &= \frac{(T_0+t)}{(T_0+\theta)} c_p(0) d\theta + [\mu(p) - (T_0+t)\mu_T(0)]dS_A \\ &= \frac{(T_0+t)}{(T_0+\theta)} c_p^0 d\Theta + \left[\mu(p) - \frac{(T_0+t)}{(T_0+\theta)} \mu(0) \right] dS_A. \end{aligned} \quad (\text{A.12.1})$$

The quantity $\mu(p)dS_A$ is now subtracted from each of these three expressions and the whole equation is then multiplied by $(T_0+\theta)/(T_0+t)$ obtaining

$$(T_0+\theta)d\eta = c_p(0) d\theta - (T_0+\theta)\mu_T(0) dS_A = c_p^0 d\Theta - \mu(0) dS_A. \quad (\text{A.12.2})$$

From this follows all the following partial derivatives between η , θ , Θ and S_A ,

$$\Theta_\theta|_{S_A} = c_p(S_A, \theta, 0)/c_p^0, \quad \Theta_{S_A}|_\theta = [\mu(S_A, \theta, 0) - (T_0+\theta)\mu_T(S_A, \theta, 0)]/c_p^0, \quad (\text{A.12.3})$$

$$\Theta_\eta|_{S_A} = (T_0+\theta)/c_p^0, \quad \Theta_{S_A}|_\eta = \mu(S_A, \theta, 0)/c_p^0, \quad (\text{A.12.4})$$

$$\theta_\eta|_{S_A} = (T_0+\theta)/c_p(S_A, \theta, 0), \quad \theta_{S_A}|_\eta = (T_0+\theta)\mu_T(S_A, \theta, 0)/c_p(S_A, \theta, 0), \quad (\text{A.12.5})$$

$$\theta_\Theta|_{S_A} = c_p^0/c_p(S_A, \theta, 0), \quad \theta_{S_A}|_\Theta = -[\mu(S_A, \theta, 0) - (T_0+\theta)\mu_T(S_A, \theta, 0)]/c_p(S_A, \theta, 0), \quad (\text{A.12.6})$$

$$\eta_\theta|_{S_A} = c_p(S_A, \theta, 0)/(T_0+\theta), \quad \eta_{S_A}|_\theta = -\mu_T(S_A, \theta, 0), \quad (\text{A.12.7})$$

$$\eta_\Theta|_{S_A} = c_p^0/(T_0+\theta), \quad \eta_{S_A}|_\Theta = -\mu(S_A, \theta, 0)/(T_0+\theta). \quad (\text{A.12.8})$$

The three second order derivatives of $\hat{\eta}(S_A, \Theta)$ are listed in Eqns. (P.14) and (P.15) of appendix P. The corresponding derivatives of $\hat{\theta}(S_A, \Theta)$, namely $\hat{\theta}_\Theta$, $\hat{\theta}_{S_A}$, $\hat{\theta}_{\Theta\Theta}$, $\hat{\theta}_{S_AS_A}$ and $\hat{\theta}_{S_A\Theta}$ can also be derived using Eqn. (P.13), obtaining

$$\hat{\theta}_\Theta = \frac{1}{\tilde{\Theta}_\theta}, \quad \hat{\theta}_{S_A} = -\frac{\tilde{\Theta}_{S_A}}{\tilde{\Theta}_\theta}, \quad \hat{\theta}_{\Theta\Theta} = -\frac{\tilde{\Theta}_{\theta\theta}}{(\tilde{\Theta}_\theta)^3}, \quad \hat{\theta}_{S_A\Theta} = -\frac{\tilde{\Theta}_{\theta S_A}}{(\tilde{\Theta}_\theta)^2} + \frac{\tilde{\Theta}_{S_A}\tilde{\Theta}_{\theta\theta}}{(\tilde{\Theta}_\theta)^3}, \quad (\text{A.12.9a,b,c,d})$$

$$\text{and } \hat{\theta}_{S_AS_A} = -\frac{\tilde{\Theta}_{S_AS_A}}{\tilde{\Theta}_\theta} + 2\frac{\tilde{\Theta}_{S_A}}{\tilde{\Theta}_\theta}\frac{\tilde{\Theta}_{\theta S_A}}{\tilde{\Theta}_\theta} - \left(\frac{\tilde{\Theta}_{S_A}}{\tilde{\Theta}_\theta}\right)^2\frac{\tilde{\Theta}_{\theta\theta}}{\tilde{\Theta}_\theta}, \quad (\text{A.12.10})$$

in terms of the partial derivatives $\tilde{\Theta}_\theta$, $\tilde{\Theta}_{S_A}$, $\tilde{\Theta}_{\theta\theta}$, $\tilde{\Theta}_{\theta S_A}$ and $\tilde{\Theta}_{S_AS_A}$ which can be obtained by differentiating the polynomial $\tilde{\Theta}(S_A, \theta)$ from the TEOS-10 Gibbs function.