

## Notes on the function gsw\_enthalpy\_second\_derivatives(SA,CT,p)

This function, **gsw\_enthalpy\_second\_derivatives**(SA,CT,p), evaluates the second order partial derivatives of enthalpy  $h = \hat{h}(S_A, \Theta, p)$ , with respect to Absolute Salinity and Conservative Temperature,  $\hat{h}_{\Theta\Theta}$ ,  $\hat{h}_{S_A\Theta}$  and  $\hat{h}_{S_A S_A}$ , as derived by McDougall *et al.* (2011), and as given in Eqns. (A.11.19) – (A.11.21) of the TEOS-10 Manual (IOC *et al.*, 2010), repeated here.

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

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

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

The first steps in the present function **gsw\_enthalpy\_second\_derivatives**(SA,CT,p) are to calculate *in situ* temperature  $t$  and potential temperature  $\theta$ . This function evaluates the above three expressions directly from the various partial derivatives of 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.

$\hat{h}_{\Theta\Theta}$  is naturally well-behaved as Absolute Salinity approaches zero, as well as at  $S_A = 0 \text{ g kg}^{-1}$ .  $\hat{h}_{S_A\Theta}$  is well-behaved as Absolute Salinity approaches zero, but the expression (A.11.20) returns a Nan when  $S_A < 10^{-330} \text{ g kg}^{-1}$ . This is avoided by trapping values  $S_A$  less than  $10^{-100} \text{ g kg}^{-1}$  and replacing them with  $10^{-100} \text{ g kg}^{-1}$  before Eqn. (A.11.20) is evaluated.  $\hat{h}_{S_A S_A}$  has an unavoidable, physically realistic singularity that scales as  $S_A^{-0.5}$  as  $S_A$  approaches zero.

## 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](http://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., P. M. Barker, D. R. Jackett, C. Roberts-Thomson, R. Feistel and R. W. Hallberg, 2011: A computationally efficient 48-term expression for the density of seawater in terms of Conservative Temperature, and related properties of seawater. submitted to *Ocean Science Discussions*.

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  $\mu$  to be functions of entropy  $\eta$  (in place of temperature  $t$ ), that is, considering the functional form of  $h$  and  $\mu$  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  $\eta$  is simply a function of Absolute Salinity  $S_A$  and potential temperature  $\theta$ , 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  $\Theta$  may also be expressed as a function of only  $S_A$  and  $\eta$ . It follows that  $\Theta$  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  $\eta$ ,  $\theta$  and  $\Theta$  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

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

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

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

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

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

so that

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

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

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

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

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

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  $p_r = 0$ )

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

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

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

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

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

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

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

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

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

The partial derivative  $\hat{h}_{\Theta}$  follows directly from this equation as

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

At  $p = 0$  this equation reduces to

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

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

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

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))

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

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

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

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

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

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  $\hat{h}_{\Theta}$  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  $\hat{h}_{S_A S_A}$  can be written in terms of the seawater Gibbs function as (from McDougall *et al.* (2011b))

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

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

and

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

These second order partial derivatives can be calculated using the GSW Oceanographic Toolbox function **gsw\_enthalpy\_second\_derivatives**.

### A.12 Differential relationships between $\eta$ , $\theta$ , $\Theta$ 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  $\eta$ ,  $\theta$ ,  $\Theta$  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  $\hat{\theta}_\Theta$ ,  $\hat{\theta}_{S_A}$ ,  $\hat{\theta}_{\Theta\Theta}$ ,  $\hat{\theta}_{S_A\Theta}$  and  $\hat{\theta}_{S_A S_A}$  can also be derived using Eqn. (P.13), obtaining

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

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

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