Notes on the first and second order 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 Conservative Temperature Θ.

We begin by noting that the three standard derivatives of $h = h(S_{\mathrm{A}}, t, p)$ when *in situ* temperature t is taken as the "temperature-like" variable are

$$\partial h/\partial S_{\mathrm{A}}\big|_{T,p} = \mu(S_{\mathrm{A}},t,p) - (T_0+t)\,\mu_T(S_{\mathrm{A}},t,p), \tag{1}$$

$$\partial h/\partial T\big|_{S_{\mathrm{A}},p} = c_p(S_{\mathrm{A}},t,p) = (T_0+t)\,\eta_T(S_{\mathrm{A}},t,p), \tag{2}$$

and

$$\partial h/\partial P\big|_{S_{\mathrm{A}},T} = v(S_{\mathrm{A}},t,p) - (T_0+t)\,v_T(S_{\mathrm{A}},t,p). \tag{3}$$

Now considering specific enthalpy to be a function of entropy (rather than of temperature t), that is, taking $h = \tilde{h}(S_{\mathrm{A}},\eta,p)$, the fundamental thermodynamic relation (Eqn. (A.7.1) of IOC *et al*. (2010)) becomes

$$\tilde{h}_\eta\,\mathrm{d}\eta + \tilde{h}_{S_{\mathrm{A}}}\mathrm{d}S_{\mathrm{A}} = (T_0+t)\,\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}} \quad \text{while} \quad \partial\tilde{h}/\partial P\big|_{S_{\mathrm{A}},\eta} = v, \tag{4}$$

so that

$$\partial\tilde{h}/\partial\eta\big|_{S_{\mathrm{A}},p} = (T_0+t) \qquad \text{and} \qquad \partial\tilde{h}/\partial S_{\mathrm{A}}\big|_{\eta,p} = \mu. \tag{5}$$

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

$$\hat{h}_\Theta\,\mathrm{d}\Theta + \hat{h}_{S_{\mathrm{A}}}\mathrm{d}S_{\mathrm{A}} = (T_0+t)\,\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}} \qquad \text{while} \qquad \partial\hat{h}/\partial P\big|_{S_{\mathrm{A}},\Theta} = v. \tag{6}$$

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

$$\hat{h}_\Theta\big|_{S_{\mathrm{A}},p} = (T_0+t)\,\eta_\Theta\big|_{S_{\mathrm{A}},p} = (T_0+t)\,\eta_\Theta\big|_{S_{\mathrm{A}}}. \tag{7}$$

At $p=0$ this equation reduces to

$$\hat{h}_\Theta\big|_{S_{\mathrm{A}},p=0} = c_p^0 = (T_0+\theta)\,\eta_\Theta\big|_{S_{\mathrm{A}}}, \tag{8}$$

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

$$\boxed{\hat{h}_\Theta\big|_{S_{\mathrm{A}},p} = \frac{(T_0+t)}{(T_0+\theta)}\,c_p^0.} \tag{9}$$

To evaluate the $\hat{h}_{S_{\mathrm{A}}}$ partial derivative we first write h in the functional form $h = \tilde{h}\big(S_{\mathrm{A}},\eta(S_{\mathrm{A}},\Theta),p\big)$ and then differentiate it, finding (using both parts of Eqn. (5))

$$\hat{h}_{S_{\mathrm{A}}}\big|_{\Theta,p} = \mu(S_{\mathrm{A}},t,p) + (T_0+t)\,\eta_{S_{\mathrm{A}}}\big|_\Theta. \tag{10}$$

The differential expression Eqn. (6) can be evaluated at $p=0$ where the left-hand side is simply $c_p^0\mathrm{d}\Theta$ so that from Eqn. (6) we find that

$$\eta_{S_{\mathrm{A}}}\big|_\Theta = -\,\frac{\mu(S_{\mathrm{A}},\theta,0)}{(T_0+\theta)}, \tag{11}$$

so that the desired expression for $\hat{h}_{S_{\mathrm{A}}}$ is

$$\boxed{\hat{h}_{S_{\mathrm{A}}}\big|_{\Theta,p} = g_{S_{\mathrm{A}}}(S_{\mathrm{A}},t,p) - \frac{(T_0+t)}{(T_0+\theta)}\,g_{S_{\mathrm{A}}}(S_{\mathrm{A}},\theta,0).} \tag{12}$$

The above boxed expressions for two isobaric derivatives of specific enthalpy are important as they are integral to forming the First Law of Thermodynamics in terms of Conservative Temperature.

In order to find the desired expression for $\hat{h}_{\Theta\Theta}\big|_{S_{\mathrm{A}},p}$ we first need an expression for $\partial\Theta/\partial T\big|_{S_{\mathrm{A}},p}$ and $\partial\Theta/\partial\theta\big|_{S_{\mathrm{A}}}$. These are found by differentiating with respect to *in situ* temperature the entropy equality $\eta\left(S_{\mathrm{A}},t,p\right)=\hat{\eta}\left(S_{\mathrm{A}},\Theta\left[S_{\mathrm{A}},t,p\right]\right)$ obtaining (using the relation $\hat{\eta}_{\Theta}\big|_{S_{\mathrm{A}}}=c_p^0/\left(T_0+\theta\right)$ from Eqn. (8) above)

$$\left.\frac{\partial\Theta}{\partial T}\right|_{S_{\mathrm{A}},p} = \eta_T\left(S_{\mathrm{A}},t,p\right)\left.\frac{\partial\Theta}{\partial\eta}\right|_{S_{\mathrm{A}}} = -\left(T_0+\theta\right)\frac{g_{TT}\left(S_{\mathrm{A}},t,p\right)}{c_p^0}\ , \tag{13}$$

and when this is evaluated at $p = 0$ dbar we find

$$\left.\frac{\partial\Theta}{\partial\theta}\right|_{S_{\mathrm{A}}} = -\left(T_0+\theta\right)\frac{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)}{c_p^0}\ . \tag{14}$$

Differentiating the expression (9) for $\hat{h}_{\Theta}$ with respect to Θ using Eqns. (13) and (14) then yields

$$\boxed{h_{\Theta\Theta}\big|_{S_{\mathrm{A}},p} = \hat{h}_{\Theta\Theta} = \frac{\left(c_p^0\right)^2}{\left(T_0+\theta\right)^2}\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{1}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{1}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\right).} \tag{15}$$

To obtain the expression for $\hat{h}_{S_{\mathrm{A}}\Theta}$ we start with the expression (12) for $\hat{h}_{S_{\mathrm{A}}}\big|_{\Theta,p}$ and differentiate it with respect to Θ using Eqns. (13) and (14), giving

$$\boxed{\begin{aligned}\hat{h}_{S_{\mathrm{A}}\Theta} = {} & \frac{c_p^0}{\left(T_0+\theta\right)}\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},\theta,0\right)}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},t,p\right)}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\right)\\ & - \frac{c_p^0\, g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)^2}\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{1}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{1}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\right).\end{aligned}} \tag{16}$$

To obtain the expression for $\hat{h}_{S_{\mathrm{A}}S_{\mathrm{A}}}$ we again start with the expression (12) for $\hat{h}_{S_{\mathrm{A}}}\big|_{\Theta,p}$ and differentiate it with respect to S_{A} at constant Θ and p. We will operate differently on the first and second parts of the right-hand side of Eqn. (12). The first part, namely $g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},t,p\right)$, will be differentiated using the relation (based on regarding φ as $\varphi\left(S,\,t\left[S_{\mathrm{A}},\Theta,p\right],p\right)$)

$$\left.\frac{\partial\varphi}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} = \left.\frac{\partial\varphi}{\partial S_{\mathrm{A}}}\right|_{T,p} + \left.\frac{\partial\varphi}{\partial T}\right|_{S_{\mathrm{A}},p}\left.\frac{\partial T}{\partial S_{\mathrm{A}}}\right|_{\Theta,p}, \tag{17}$$

while for the second part of Eqn. (12) we will use the relation (based on regarding φ as $\varphi\left(S_{\mathrm{A}},\,\theta\left[S_{\mathrm{A}},\Theta\right],p\right)$)

$$\left.\frac{\partial\varphi}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} = \left.\frac{\partial\varphi}{\partial S_{\mathrm{A}}}\right|_{\theta,p} + \left.\frac{\partial\varphi}{\partial\theta}\right|_{S_{\mathrm{A}},p}\left.\frac{\partial\theta}{\partial S_{\mathrm{A}}}\right|_{\Theta}. \tag{18}$$

From the identity $d\Theta = \Theta_{S_{\mathrm{A}}}\,dS_{\mathrm{A}} + \Theta_T\,dT + \Theta_p\,dp$ we find that

$$\left.\frac{\partial T}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} = -\frac{\partial\Theta/\partial S_{\mathrm{A}}\big|_{T,p}}{\partial\Theta/\partial T\big|_{S_{\mathrm{A}},p}}\ . \tag{19}$$

We have Eqn. (13) for $\partial\Theta/\partial T\big|_{S_{\mathrm{A}},p}$ and we can find the expression for $\partial\Theta/\partial S_{\mathrm{A}}\big|_{T,p}$ by differentiating with respect to Absolute Salinity the entropy equality

$\eta\left(S_{\mathrm{A}},t,p\right)=\hat{\eta}\left(S_{\mathrm{A}},\Theta\left[S_{\mathrm{A}},t,p\right]\right)$ obtaining (using the relations $\hat{\eta}_{\Theta}\big|_{S_{\mathrm{A}}}=c_p^0\big/\left(T_0+\theta\right)$ and $\hat{\eta}_{S_{\mathrm{A}}}\big|_{\Theta}=-g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\big/\left(T_0+\theta\right)$ from Eqns. (8) and (11) above)

$$\left.\frac{\partial\Theta}{\partial S_{\mathrm{A}}}\right|_{T,p} = \frac{\left[\eta_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},t,p\right)-\hat{\eta}_{S_{\mathrm{A}}}\big|_{\Theta}\right]}{\hat{\eta}_{\Theta}\big|_{S_{\mathrm{A}}}} = \frac{\left[g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)-\left(T_0+\theta\right)g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},t,p\right)\right]}{c_p^0}. \tag{20}$$

Substituting this into Eqn. (19) we find

$$\left.\frac{\partial T}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} = \frac{\left[g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)-\left(T_0+\theta\right)g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},t,p\right)\right]}{\left(T_0+\theta\right)g_{TT}\left(S_{\mathrm{A}},t,p\right)}. \tag{21}$$

When this is evaluated at $p=0$ dbar we find

$$\left.\frac{\partial\theta}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} = \left.\frac{\partial\theta}{\partial S_{\mathrm{A}}}\right|_{\Theta} = -\frac{\Theta_{S_{\mathrm{A}}}\big|_{\theta,p}}{\Theta_{\theta}\big|_{S_{\mathrm{A}},p}} = -\frac{\tilde{\Theta}_S}{\tilde{\Theta}_\theta} = \frac{\left[g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)-\left(T_0+\theta\right)g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},\theta,0\right)\right]}{\left(T_0+\theta\right)g_{TT}\left(S_{\mathrm{A}},\theta,0\right)}. \tag{22}$$

Differentiating the two parts of Eqn. (12) differently as described above, and using Eqns. (17), (18), (21) and (22) leads to the following expression for $\hat{h}_{S_{\mathrm{A}}S_{\mathrm{A}}}$

$$\boxed{\begin{aligned}\hat{h}_{S_{\mathrm{A}}S_{\mathrm{A}}} &= g_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(S_{\mathrm{A}},t,p\right) - \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}g_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\\ &+ \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{\left[g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},\theta,0\right)\right]^2}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{\left[g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},t,p\right)\right]^2}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\\ &- \frac{2\,g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)}\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},\theta,0\right)}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{g_{S_{\mathrm{A}}T}\left(S_{\mathrm{A}},t,p\right)}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\right)\\ &+ \frac{\left[g_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\right]^2}{\left(T_0+\theta\right)^2}\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\frac{1}{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)} - \frac{1}{g_{TT}\left(S_{\mathrm{A}},t,p\right)}\right).\end{aligned}} \tag{23}$$

These first and second order partial derivatives can also be written as pressure integrals, using the following procedure. First write enthalpy $h=\hat{h}\left(S_{\mathrm{A}},\Theta,p\right)$ in terms of potential enthalpy, $h^0\equiv c_p^0\,\Theta$, using the definition of potential enthalpy (Eqn. (3.2.1) of IOC *et al*. (2010))

$$h = \hat{h}\left(S_{\mathrm{A}},\Theta,p\right) = c_p^0\,\Theta + \int_{P_0}^{P}\hat{v}\left(S_{\mathrm{A}},\Theta,p'\right)dP'. \tag{24}$$

Differentiating this with respect to Θ gives

$$h_{\Theta}\big|_{S_{\mathrm{A}},p} = \hat{h}_{\Theta} = c_p^0 + \int_{P_0}^{P}\alpha^{\Theta}\big/\rho\ dP' \approx c_p^0 + \tfrac{1}{\rho_0}\int_{P_0}^{P}\alpha^{\Theta}\ dP', \tag{25}$$

where ρ_0 is a constant density of 1035 $\mathrm{kg\ m^{-3}}$. Similarly we have

$$h_{S_{\mathrm{A}}}\big|_{\Theta,p} = \hat{h}_{S_{\mathrm{A}}} = -\int_{P_0}^{P}\beta^{\Theta}\big/\rho\ dP' \approx -\tfrac{1}{\rho_0}\int_{P_0}^{P}\beta^{\Theta}\ dP'. \tag{26}$$

The second order partial derivatives can be found in a similar manner as

$$\hat{h}_{\Theta\Theta} = \int_{P_0}^{P}\hat{v}_{\Theta\Theta}\ dP' = \int_{P_0}^{P}\left(\alpha^{\Theta}\big/\rho\right)_{\Theta}\ dP', \tag{27}$$

$$\hat{h}_{S_A\Theta} \;=\; \int_{P_0}^{P} \hat{v}_{S_A\Theta} \; dP' \;=\; \int_{P_0}^{P} \left(\alpha^{\Theta}/\rho\right)_{S_A} \; dP' \;\;=\; -\int_{P_0}^{P} \left(\beta^{\Theta}/\rho\right)_{\Theta} \; dP', \tag{28}$$

$$\hat{h}_{S_A S_A} \;=\; \int_{P_0}^{P} \hat{v}_{S_A S_A} \; dP' \;=\; -\int_{P_0}^{P} \left(\beta^{\Theta}/\rho\right)_{S_A} \; dP' \quad . \tag{29}$$