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

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

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

and

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

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

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

so that

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

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

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

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

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

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 $p_r = 0$)

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

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

$$\boxed{\tilde{h}_\theta\big|_{S_A, p} = c_p(S_A, \theta, 0)\frac{(T_0 + t)}{(T_0 + \theta)}.} \tag{A.11.9}$$

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

$$\tilde{h}_{S_A}\big|_{\theta, p} = \hat{h}_{S_A}\big|_{\eta, p} + \hat{h}_\eta\big|_{S_A, p}\eta_{S_A}\big|_\theta. \tag{A.11.10}$$

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

$$\boxed{\tilde{h}_{S_A}\big|_{\theta, p} = \mu(S_A, t, p) - (T_0 + t)\mu_T(S_A, \theta, 0).} \tag{A.11.11}$$

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

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

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

$$\left. \hat{h}_\Theta \right|_{S_A, p} \;=\; (T_0 + t) \left. \eta_\Theta \right|_{S_A, p} \;=\; (T_0 + t) \left. \eta_\Theta \right|_{S_A}. \tag{A.11.13}$$

At $p = 0$ this equation reduces to

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

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

$$\boxed{\left. \hat{h}_\Theta \right|_{S_A, p} \;=\; \frac{(T_0 + t)}{(T_0 + \theta)} \, c_p^0.} \tag{A.11.15}$$

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))

$$\left. \hat{h}_{S_A} \right|_{\Theta, p} \;=\; \mu(S_A, t, p) + (T_0 + t) \left. \eta_{S_A} \right|_\Theta. \tag{A.11.16}$$

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

$$\left. \eta_{S_A} \right|_\Theta \;=\; -\frac{\mu(S_A, \theta, 0)}{(T_0 + \theta)}, \tag{A.11.17}$$

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

$$\boxed{\left. \hat{h}_{S_A} \right|_{\Theta, p} \;=\; \mu(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(S_A, \theta, 0).} \tag{A.11.18}$$

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.