

## 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  $\hat{\theta}_\Theta$ ,  $\hat{\theta}_{S_A}$ ,  $\hat{\theta}_{\Theta\Theta}$ ,  $\hat{\theta}_{S_AS_A}$  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.

### ... and an excerpt from appendix P

The partial derivatives with respect to  $\Theta$  and with respect to  $\theta$ , both at constant  $S_A$  and  $p$ , and the partial derivatives with respect to  $S_A$ , are related by

$$\frac{\partial}{\partial \Theta}\bigg|_{S_A, p} = \frac{1}{\tilde{\Theta}_\theta} \frac{\partial}{\partial \theta}\bigg|_{S_A, p}, \quad \text{and} \quad \frac{\partial}{\partial S_A}\bigg|_{\Theta, p} = \frac{\partial}{\partial S_A}\bigg|_{\theta, p} - \frac{\tilde{\Theta}_{S_A}}{\tilde{\Theta}_\theta} \frac{\partial}{\partial \theta}\bigg|_{S_A, p}. \quad (\text{P.13a,b})$$

Use of these expressions, acting on entropy yields (with  $p = 0$  everywhere, and using Eqn. (P.7) [or Eqn. (A.12.8b)] and Eqn. (P.8))

$$\hat{\eta}_{\Theta} = \frac{\tilde{\eta}_{\theta}}{\tilde{\Theta}_{\theta}} \equiv \frac{c_p^0}{(T_0 + \theta)}, \quad \hat{\eta}_{\Theta\Theta} = -\frac{1}{\tilde{\Theta}_{\theta}} \frac{c_p^0}{(T_0 + \theta)^2}, \quad \hat{\eta}_{S_A} = -\frac{\tilde{\mu}(S_A, \theta, 0)}{(T_0 + \theta)}, \quad (\text{P.14a,b,c})$$

$$\hat{\eta}_{S_A\Theta} = \frac{\tilde{\Theta}_{S_A}}{\tilde{\Theta}_{\theta}} \frac{c_p^0}{(T_0 + \theta)^2}, \quad \text{and} \quad \hat{\eta}_{S_AS_A} = -\frac{\tilde{\mu}_{S_A}(S_A, \theta, 0)}{(T_0 + \theta)} - \frac{(\tilde{\Theta}_{S_A})^2}{\tilde{\Theta}_{\theta}} \frac{c_p^0}{(T_0 + \theta)^2}, \quad (\text{P.15a,b})$$

in terms of the partial derivatives of the exact polynomial expressions (P.11b) and (P.12).