Isentropic Thermal Pressure Coefficient

The volume of a given closed system is defined by the following set of independent variables where $\xi$ is the general composition variable.

$$V = V[T, p, \xi^\text{eq}; A = 0] \quad (a)$$

We have rather over-defined the system. The aim is to identify the composition variable at equilibrium and the condition that the affinity for spontaneous change is zero. The dependent variable entropy for this system is defined in analogous fashion; equation (b).

$$S = S[T, p, \xi^\text{eq}; A = 0] \quad (b)$$

The system is perturbed by a change in temperature along a path for which the affinity for spontaneous change is zero. Moreover the entropy of the system remains the same as that given in equation (b). In order to hold the latter condition the equilibrium pressure must change. In the state defined by the independent variables $[T, p, \xi^\text{eq}; A = 0]$ the (equilibrium) isentropic differential dependence of pressure $p$ on temperature is the isentropic thermal pressure coefficient, $\beta_S$; equation (c).

$$\beta_S = (\partial p / \partial T)_S \quad (c)$$

Further [1] $\beta_S = (\partial S / \partial V)_T$ (d)

Also [2], $\beta_S = \sigma / (T \cdot \alpha_p)$ (e)

Here $\sigma$ is the isobaric heat capacity for unit volume (heat capacitance) of the system, $C_p / V$. The three isentropic properties $\alpha_s, \kappa_s$ and $\beta_s$ are related using equation (f); [3].

$$\beta_s = -\alpha_s / \kappa_s \quad (f)$$

With reference to the (equilibrium) thermal expansivity, $\alpha_s$, we envisage that the temperature is changed to produce a change in volume along a path for which the entropy remains the same as in equation (b) and the affinity for spontaneous change remains at zero.

$$\alpha_s (A = 0) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{S; A=0} \quad (g)$$
In analogous fashion, $\kappa_S$ is a measure of the change in volume produced by a change in pressure.

$$\kappa_S(A = 0) = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{S,A=0} \tag{h}$$

**Footnotes**

[1] From $\left[ \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial S} \right) \right]_p |_S = \left[ \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial p} \right) \right]_p |_S$

But at equilibrium where $A = 0$, $T = \left( \frac{\partial H}{\partial S} \right)_p |_S$ and $V = \left( \frac{\partial H}{\partial p} \right)_S$

Then $\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p$. From $\beta_S = \left( \frac{\partial p}{\partial T} \right)_S$.

Using the above Maxwell Relation, $\beta_S = \left( \frac{\partial S}{\partial V} \right)_T$

[2] From the definition, $\beta_S = \left( \frac{\partial p}{\partial T} \right)_S$

Using a calculus operation $\beta_S = \left( \frac{\partial S}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial S} \right)_T$

From the Gibbs-Helmholtz Equation, $\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$

From a Maxwell equation, $\left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial V}{\partial T} \right)_p$. Then $\beta_S = \frac{C_p}{T} \cdot \frac{1}{E_p}$

But $E_p = V \cdot \alpha_p$. Then $\beta_S = \frac{C_p}{V} \cdot \frac{1}{T \cdot \alpha_p}$ Or, $\beta_S = \sigma / T \cdot \alpha_p$

[3] From the definition, $\beta_S = \left( \frac{\partial p}{\partial T} \right)_S$, then $\beta_S = \left( \frac{\partial p}{\partial V} \right)_S \cdot \left( \frac{\partial V}{\partial T} \right)_S$

Then $\beta_S = -E_s / K_s = -(E_s / V) / (K_s / V) = -\alpha_s / \kappa_s$

Also from [2] and [3], $E_s / K_s = \frac{C_p}{V} \cdot \frac{1}{T \cdot \alpha_p}$

Then $\alpha_s / \kappa_s = -\sigma / T \cdot \alpha_p$