Expansibilities; Isobaric and Isentropic

Equilibrium isentropic and isobaric expansibilities are defined in terms of the corresponding expansions.

\[
\alpha_s(A=0) = E_s(A=0)/V \\
\alpha_p(A=0) = E_p(A=0)/V
\]

The difference between these expansibilities defines a property \( \varepsilon \);
equation (c). [1]

\[
\varepsilon = \alpha_p(A=0) - \alpha_s(A=0) \tag{c}
\]

Then [1], \( \varepsilon = \kappa_T \cdot \sigma / T \cdot \alpha_p \) (d)

The property \( \alpha_s(A=0) \) has been said to be ‘of little importance’ [2]. In fact it is common practice to omit the subscript ‘p’ and use the symbol \( \alpha \) to represent the (equilibrium) isobaric expansibility.

Footnotes

[1] From a calculus operation

\[
\left( \frac{\partial V}{\partial T} \right)_S = \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial S}{\partial T} \right)_p \left( \frac{\partial p}{\partial V} \right)_T
\]

Using a Maxwell relation \( \left( \frac{\partial p}{\partial S} \right)_T = - \left( \frac{\partial T}{\partial p} \right)_T \) so that \( E_p = - \left( \frac{\partial S}{\partial p} \right)_T \)

But isothermal compression, \( K_T = - \left( \frac{\partial V}{\partial p} \right)_T \). Also \( C_p = T \cdot \left( \frac{\partial S}{\partial T} \right)_p \)

Then \( E_s = E_p - \frac{C_p}{T} \cdot \left( \frac{1}{E_p} \right) \cdot (-K_T) \)

By definition, \( \sigma = \frac{C_p}{V} \) and \( \kappa_T = \frac{K_T}{V} \)

Hence, \( \alpha_s = \alpha_p - \kappa_T \cdot \sigma / T \cdot \alpha_p \). By definition, \( \varepsilon = \alpha_p - \alpha_s \)

Hence, \( \varepsilon = \kappa_T \cdot \sigma / T \cdot \alpha_p \)