Entropy: Dependence on Temperature and Pressure

The volume of a given closed system at equilibrium prepared using \( n_1 \) moles of solvent (water) and \( n_j \) moles of solute-\( j \) is defined by the set of independent variables shown in equation (a).

\[
V = V[T, p, n_1, n_j, A = 0, \xi^{eq}] \quad (a)
\]

The same set of independent variables defines the entropy \( S \).

\[
S = S[T, p, n_1, n_j, A = 0, \xi^{eq}] \quad (b)
\]

We envisage that the system is displaced by a change in pressure along a path where the system remains at equilibrium (i.e. \( A = 0 \)) and the volume remains the same as defined by equation (a). In a plot of entropy against \( p \), the gradient of the plot at the point defined by the independent variables, \( [T, p, n_1, n_j, A = 0, \xi^{eq}] \) is given by equation (c).

\[
\text{Isochoric} \quad \left( \frac{\partial S}{\partial p} \right)_{V, A=0} \quad (c)
\]

The set of derivatives is completed by the following partial derivatives.

\[
\text{Isothermal} \quad \left( \frac{\partial S}{\partial p} \right)_{T, A=0} \quad (d)
\]

\[
\text{Isobaric} \quad \left( \frac{\partial S}{\partial T} \right)_{p, A=0} \quad (e)
\]