Here’s a quick review of how the so-called Gibbs-Duhem relation is obtained in thermodynamics. Consider an extensive function like the energy of the system, \( E \). Extensive means that
\[
E(\lambda \{\text{extensive variables}\}, \{\text{intensive variables}\}) = \lambda E(\{\text{extensive variables}\}, \{\text{intensive variables}\}),
\]
where \( \lambda \) is arbitrary. For example, consider the energy as a function of the entropy, \( S \), volume, \( V \), and number of moles or molecules, \( N \) (for a one component system); Since each of these is extensive, and can be used to specify state of a one-component system, Eq. (1) implies that
\[
E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N).
\]
By differentiating both sides with respect to lambda, and evaluating the result at \( \lambda = 1 \) we get:
\[
S \left( \frac{\partial E}{\partial S} \right)_{V,N} + V \left( \frac{\partial E}{\partial V} \right)_{S,N} + N \left( \frac{\partial E}{\partial N} \right)_{S,V} = E(S, V, N).
\]
If we combine the first and second laws of thermodynamics we can write
\[
dE = TdS - pdV + \mu dN,
\]
where \( T \), \( p \), and \( \mu \) are the absolute temperature, pressure, and chemical potential, respectively. When this is used to evaluate the derivatives appearing on the left hand side of Eq. (3) it follows that
\[
E(S, V, N) = TS - pV + \mu N.
\]

By taking the differential of Eq. (5) we see that
\[
dE = TdS + SdT - pdV - Vdp + \mu dN + 2d\mu,
\]
which when compared with Eq. (4) implies that
\[
0 = SdT - Vdp + Nd\mu.
\]
This is known as the Gibbs-Duhem relation, and implies that changes in the intensive quantities are not independent. In particular, it implies that
\[
\left( \frac{\partial \mu}{\partial p} \right)_T = \frac{V}{N} \equiv \bar{V}
\]
and
\[
\left( \frac{\partial \mu}{\partial T} \right)_p = -\frac{S}{N} \equiv \bar{S}.
\]

How does this discussion generalize for mixtures? Show that for any extensive quantity \( A(T, p, N_1, N_2, \ldots) \),
\[ A(T, p, N_1, N_2, \ldots) = N_1 \bar{A}_1 + N_2 \bar{A}_2 + \ldots \quad (10) \]

where

\[ \bar{A}_i \equiv \left( \frac{\partial A}{\partial N_i} \right)_{T, p, N_{\neq i}} \quad (11) \]

is a partial molar quantity.