Mixture Equation of State

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§1 Induction

Suppose given $V = \sum x_j V_j(T, P_j) = \sum x_j V_j(T, P_{base} + \Delta P_j)$, we let $\chi_j = \frac{x_j}{1-x_c}$ for $1 \leq j < c$ so $\sum \chi_j = 1$. Then, define $\mathcal{V}$ and $\mathcal{F}$ to be

$$\mathcal{V}(T, P_{base}) = \sum \chi_j V_j(T, P_j) = \sum \chi_j V_j(T, P_{base} + \Delta P_j) \tag{1}$$

$$\mathcal{F}(T, P_{base}) = \sum \chi_j F_j \left(T, \frac{M_j}{V_j(T, P_{base} + \Delta P_j)}\right) + \mathcal{C}T \tag{2}$$

where $\mathcal{C}$ is some constant.

I place emphasis on the fact that $\mathcal{V}, \mathcal{F}$ are defined such that the P_{base} of V, F and that of $\mathcal{V}, \mathcal{F}$ are equal. Since equations either represent a shift in Degrees of Freedom, or a resolution of conflict thereof, in (1) we choose not to write P_j or P_{base} as a function of $\mathcal{V}$ to avoid an equation equivalent to $\mathcal{V} = \mathcal{V}$. Suffice it to say P_j is still a function of $\mathcal{V}, T$ since $\mathcal{V}$ is a function of T, P_j. However, note that it is dangerous to use the notation $P_j = P_j(T, \mathcal{V})$ and $P_j = P_j(T, V)$ to represent P_j as a function of either because $\{P_j(T, k) \mid k = \mathcal{V}\} \neq \{P_j(T, k) \mid k = V\}$. It follows that

$$\begin{aligned}
V(T, P_{base}) &= \sum x_j V_j(T, P_{base} + \Delta P_j) \\
&= x_c V_c(T, P_{base} + \Delta P_c) + \sum^{c-1} x_j V_j(T, P_{base} + \Delta P_j) \\
&= x_c V_c(T, P_{base} + \Delta P_c) + (1 - x_c) \sum \chi_j V_j(T, P_{base} + \Delta P_j) \\
&= x_c V_c(T, P_{base} + \Delta P_c) + (1 - x_c)\mathcal{V}(T, P_{base}) \qquad (3)
\end{aligned}$$

$$\begin{aligned}
F(T, P_{base}) &= \sum x_j F_j \left(T, \frac{M_j}{V_j(T, P_{base} + \Delta P_j)}\right) + \mathcal{C}T \\
&= x_c F_c \left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right) + \sum^{c-1} x_j F_j \left(T, \frac{M_j}{V_j(T, P_{base} + \Delta P_j)}\right) + \mathcal{C}T \\
&= x_c F_c \left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right) + (1 - x_c) \sum \chi_j F_j \left(T, \frac{M_j}{V_j(T, P_{base} + \Delta P_j)}\right) + \mathcal{C}T \\
&= x_c F_c \left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right) + (1 - x_c)\mathcal{F}(T, P_{base}) + \mathcal{C}T \qquad (4)
\end{aligned}$$

Allowing $\mathcal{P} = -\left(\frac{\partial \mathcal{F}}{\partial \mathcal{V}}\right)_T$ and $\mathcal{E} = -T^2 \left(\frac{\partial(\mathcal{F}/T)}{\partial T}\right)_{\mathcal{V}}$, we can write

$$\mathcal{P} = \frac{1}{\sum \frac{\chi_j V_j}{B_j}} \sum \left(\frac{\chi_j V_j}{B_j}\right) P_j = \frac{1-x_c}{\sum^{c-1} \frac{x_j V_j}{B_j}} \sum^{c-1} \left(\frac{1}{1-x_c} \frac{x_j V_j}{B_j}\right) P_j = \frac{1}{\sum^{c-1} \frac{x_j V_j}{B_j}} \cdot \sum^{c-1} \left(\frac{x_j V_j}{B_j}\right) P_j \tag{5}$$

$$\mathcal{E} = \sum \chi_j E_j = \frac{1}{1-x_c} \sum^{c-1} x_j E_j \tag{6}$$

by induction hypothesis, where $B_j = -V_j \left(\frac{\partial P_j}{\partial V_j}\right)_T \Rightarrow \left(\frac{\partial V_j}{\partial P_j}\right)_T = -\frac{V_j}{B_j}$. Then we expanding $P = -\left(\frac{\partial F}{\partial V}\right)_T$ we get

$$\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_T \\
&= -\left(\frac{\partial}{\partial V}\left(x_c F_c\left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right) + (1-x_c)\mathcal{F} + \mathcal{C}T\right)\right)_T \\
&= -x_c\left(\frac{\partial}{\partial V} F_c\left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right)\right)_T - (1-x_c)\left(\frac{\partial \mathcal{F}}{\partial V}\right)_T \\
&= -x_c\left(\frac{\partial F_c}{\partial V_c}\right)_T \left(\frac{\partial V_c}{\partial P_{base}}\right)_T \left(\frac{\partial P_{base}}{\partial V}\right)_T - (1-x_c)\left(\frac{\partial \mathcal{F}}{\partial \mathcal{V}}\right)_T \left(\frac{\partial \mathcal{V}}{\partial V}\right)_T \\
&= \left(\frac{\partial P_{base}}{\partial V}\right)_T \left(x_c P_c \left(\frac{\partial V_c}{\partial P_c}\right)_T + (1-x_c)\mathcal{P}\left(\frac{\partial \mathcal{V}}{\partial P_{base}}\right)_T\right) \\
&= \frac{1}{\sum x_j \left(\frac{\partial V_j}{\partial P_{base}}\right)_T} \cdot \left(x_c P_c \cdot -\frac{V_c}{B_c} + (1-x_c)\mathcal{P} \cdot \sum^{c-1} \chi_j \left(\frac{\partial V_j}{\partial P_{base}}\right)_T\right) \\
&= \frac{1}{\sum x_j \left(\frac{\partial V_j}{\partial P_j}\right)_T} \cdot \left(-\frac{x_c V_c}{B_c} \cdot P_c + \mathcal{P} \sum^{c-1} ((1-x_c)\chi_j) \left(\frac{\partial V_j}{\partial P_j}\right)_T\right) \\
&= \frac{-1}{\sum \frac{x_j V_j}{B_j}} \cdot \left(-\frac{x_c V_c}{B_c} \cdot P_c + \mathcal{P} \sum^{c-1} x_j \cdot -\frac{V_j}{B_j}\right) \\
&= \frac{1}{\sum \frac{x_j V_j}{B_j}} \cdot \left(\frac{x_c V_c}{B_c} \cdot P_c + \frac{1}{\sum^{c-1} \frac{x_j V_j}{B_j}} \cdot \sum^{c-1} \left(\frac{x_j V_j}{B_j}\right) P_j \cdot \sum^{c-1} \frac{x_j V_j}{B_j}\right) \\
&= \underline{\frac{1}{\sum \frac{x_j V_j}{B_j}} \cdot \sum \left(\frac{x_j V_j}{B_j}\right) P_j}
\end{aligned} \tag{7}$$

as desired. Expanding $E = -T^2 \left(\frac{\partial (F/T)}{\partial T}\right)_V$, we get

$$\begin{aligned}
E &= -T^2 \left(\frac{\partial (F/T)}{\partial T}\right)_V \\
&= -T^2 \left(\frac{\partial}{\partial T}\left(\frac{1}{T}\left(x_c F_c\left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right) + (1-x_c)\mathcal{F}(T, P_{base}) + \mathcal{C}T\right)\right)\right)_V \\
&= x_c \cdot -T^2 \left(\frac{\partial}{\partial T}\left(\frac{F_c\left(T, \frac{M_c}{V_c(T, P_{base} + \Delta P_c)}\right)}{T}\right)\right)_V + (1-x_c) \cdot -T^2 \left(\frac{\partial (\mathcal{F}/T)}{\partial T}\right)_V
\end{aligned}$$

$$
\begin{aligned}
&= x_c \cdot -T^2 \left(\left(\frac{\partial(F_c/T)}{\partial T} \right)_{V_c} + \left(\frac{\partial(F_c/T)}{\partial V_c} \right)_T \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_{base}} + \left(\frac{\partial V_c}{\partial P_{base}} \right)_T \cdot \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) \right) \\
&\qquad + (1 - x_c) \cdot -T^2 \left(\left(\frac{\partial(\mathcal{F}/T)}{\partial T} \right)_{\mathcal{V}} + \left(\frac{\partial(\mathcal{F}/T)}{\partial \mathcal{V}} \right)_T \left(\frac{\partial \mathcal{V}}{\partial T} \right)_V \right) \\
&= x_c E_c - x_c T^2 \left(\frac{1}{T} \left(\frac{\partial F_c}{\partial V_c} \right)_T \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} + \left(\frac{\partial V_c}{\partial P_c} \right)_T \cdot \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) \right) \\
&\qquad + (1 - x_c) \left(\mathcal{E} - T \left(\frac{\partial \mathcal{F}}{\partial \mathcal{V}} \right)_T \left(\frac{\partial \mathcal{V}}{\partial T} \right)_V \right) \\
&= x_c E_c + x_c T \cdot P_c \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} + \left(\frac{\partial V_c}{\partial P_c} \right)_T \cdot \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) + (1 - x_c) \left(\mathcal{E} + T \mathcal{P} \left(\frac{\partial \mathcal{V}}{\partial T} \right)_V \right) \\
&= x_c E_c + \sum^{c-1} x_j E_j + x_c T \cdot P_c \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) + (1 - x_c) T \mathcal{P} \left(\frac{\partial \mathcal{V}}{\partial T} \right)_V \\
&= \sum x_j E_j + T \cdot x_c P_c \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) + T \mathcal{P} \left(\frac{\partial (V - x_C V_c)}{\partial T} \right)_V \\
&= \sum x_j E_j + T \cdot x_c P_c \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) - x_c \cdot T \mathcal{P} \left(\frac{\partial V_c}{\partial T} \right)_V \\
&= \sum x_j E_j + x_c T \left(P_c \left(\frac{\partial V_c}{\partial T} \right)_{P_c} - P_c \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V - \mathcal{P} \left(\frac{\partial V_c}{\partial T} \right)_V \right)
\end{aligned} \tag{8}
$$

It then suffices to show that

$$
\left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V = \frac{\mathcal{P}}{P_c} \left(\frac{\partial V_c}{\partial T} \right)_V \tag{9}
$$

Manipulating, we get

$$
\begin{aligned}
& \left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V = \frac{\mathcal{P}}{P_c} \left(\frac{\partial V_c}{\partial T} \right)_V \\
\Rightarrow\ & \left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V = \frac{\mathcal{P}}{P_c} \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} + \left(\frac{\partial V_c}{\partial P_c} \right)_T \left(\frac{\partial P_c}{\partial T} \right)_V \right) \\
\Rightarrow\ & \left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V = \frac{\mathcal{P}}{P_c} \left(\left(\frac{\partial V_c}{\partial T} \right)_{P_c} - \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V \right) \\
\Rightarrow\ & \left(\frac{\partial V_c}{\partial T} \right)_{P_c} = \frac{V_c}{B_c} \left(\frac{\partial P_{base}}{\partial T} \right)_V \\
\Rightarrow\ & -\left(\frac{\partial P_{base}}{\partial V_c} \right)_T \left(\frac{\partial V_c}{\partial T} \right)_{P_c} = \left(\frac{\partial P_{base}}{\partial T} \right)_V \\
\Rightarrow\ & \left(\frac{\partial P_{base}}{\partial T} \right)_{V_c} = \left(\frac{\partial P_{base}}{\partial T} \right)_V \\
\Rightarrow\ & \left(\frac{\partial P_{base}}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_{V_c} = 0
\end{aligned} \tag{10}
$$

Dead end as neither are necessarily zero.

§2 Delta Shifting

The property $E = \sum x_j E_j$ is clearly true when $c = 1$, but the scenario in which there is only one pure substance can be considered as identical to a mixture of c substances with $x_1 = 1$ and $x_j = 0$

for $j > 1$. It follows that since we want $E = \sum x_j E_j$ to be true for all *c-tuples* $(x_1, x_2, x_3, \ldots)$ such that $\sum x_j = 1$ and all such tuples are achievable by making cumulative shifts of $(\ldots x_i, \ldots x_j, \ldots) \to (\ldots x_i + \delta x, \ldots x_j - \delta x, \ldots)$ that the property must hold before and after any shift. Consider *c-tuple* $(\chi_1, \chi_2, \chi_3, \ldots)$ and define $(x_1, x_2, x_3, \ldots)$ where $x_j = \chi_j$ for all $j \neq r, s$ and $(x_r, x_s) = (\chi_r + \delta\chi, \chi_s - \delta\chi)$. With these coefficients, define

$$\mathcal{V} = \sum \chi_j V_j, \qquad V = \sum x_j V_j$$

$$\mathcal{F} = \sum \chi_j F_j + \mathcal{C}T, \qquad F = \sum x_j F_j + \mathcal{C}T$$

Then, writing V, F in terms of $\mathcal{V}, \mathcal{F}$ we get

$$V = \sum x_j V_j = \delta\chi\,(V_r - V_s) + \sum \chi_j V_j = \delta\chi\,(V_r - V_s) + \mathcal{V} \tag{11}$$

$$F = \sum x_j F_j + \mathcal{C}T = \delta\chi\,(F_r - F_s) + \sum \chi_j F_j + \mathcal{C}T = \delta\chi\,(F_r - F_s) + \mathcal{F} + \mathcal{C}T \tag{12}$$

As our base case $(1, 0, 0, 0, \ldots)$ is clearly true, by induction hypothesis suppose

$$\mathcal{P} = -\left(\frac{\partial \mathcal{F}}{\partial \mathcal{V}}\right)_T = \frac{1}{\sum \frac{\chi_j V_j}{B_j}} \cdot \sum \left(\frac{\chi_j V_j}{B_j}\right) P_j \tag{13}$$

$$\mathcal{E} = -T^2 \left(\frac{\partial(\mathcal{F}/T)}{\partial T}\right)_{\mathcal{V}} = \sum \chi_j E_j \tag{14}$$

Expanding $P = -\left(\frac{\partial F}{\partial V}\right)_T$ we get

$$\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_T \\
&= -\left(\frac{\partial}{\partial V}\left(\delta\chi\,(F_r - F_s) + \mathcal{F} + \mathcal{C}T\right)\right)_T \\
&= -\delta\chi\left(\left(\frac{\partial F_r}{\partial V}\right)_T - \left(\frac{\partial F_s}{\partial V}\right)_T\right) - \left(\frac{\partial \mathcal{F}}{\partial V}\right)_T \\
&= -\delta\chi\left(\left(\frac{\partial F_r}{\partial V_r}\right)_T \left(\frac{\partial V_r}{\partial V}\right)_T - \left(\frac{\partial F_s}{\partial V_s}\right)_T \left(\frac{\partial V_s}{\partial V}\right)_T\right) - \left(\frac{\partial \mathcal{F}}{\partial \mathcal{V}}\right)_T \left(\frac{\partial \mathcal{V}}{\partial V}\right)_T \\
&= \left(\frac{\partial P_{base}}{\partial V}\right)_T \left(\delta\chi\left(P_r\left(\frac{\partial V_r}{\partial P_{base}}\right)_T - P_s\left(\frac{\partial V_s}{\partial P_{base}}\right)\right) + \mathcal{P}\left(\frac{\partial \mathcal{V}}{\partial P_{base}}\right)_T\right) \\
&= -\left(\frac{\partial P_{base}}{\partial V}\right)_T \left(\delta\chi\left(P_r \cdot \frac{V_r}{B_r} - P_s \cdot \frac{V_s}{B_s}\right) + \mathcal{P}\sum \frac{\chi_j V_j}{B_j}\right) \\
&= -\left(\frac{\partial P_{base}}{\partial V}\right)_T \left(\delta\chi\left(P_r \cdot \frac{V_r}{B_r} - P_s \cdot \frac{V_s}{B_s}\right) + \sum \left(\frac{\chi_j V_j}{B_j}\right) P_j\right) \\
&= -\left(\frac{\partial P_{base}}{\partial V}\right)_T \sum \left(\frac{x_j V_j}{B_j}\right) P_j \\
&= \underline{\frac{1}{\sum \frac{x_j V_j}{B_j}} \cdot \sum \left(\frac{x_j V_j}{B_j}\right) P_j}
\end{aligned} \tag{15}$$

as desired. Now expanding $E = -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V$ we get

$$\begin{aligned}
E &= -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V \\
&= -T^2 \left(\frac{\partial}{\partial T}\left(\frac{1}{T}(\delta\chi(F_r - F_s) + \mathcal{F} + \mathcal{C}T)\right)\right)_V \\
&= -T^2 \left(\delta\chi\left(\left(\frac{\partial(F_r/T)}{\partial T}\right)_V - \left(\frac{\partial(F_s/T)}{\partial T}\right)_V\right) + \left(\frac{\partial(\mathcal{F}/T)}{\partial T}\right)_V\right) \\
&= -T^2\delta\chi\left(\left(\frac{\partial(F_r/T)}{\partial T}\right)_{V_r} + \left(\frac{\partial(F_r/T)}{\partial V_r}\right)_T \left(\frac{\partial V_r}{\partial T}\right)_V - \left(\frac{\partial(F_s/T)}{\partial T}\right)_{V_s} - \left(\frac{\partial(F_s/T)}{\partial V_s}\right)_T \left(\frac{\partial V_s}{\partial T}\right)_V\right) \\
&\qquad - T^2\left(\left(\frac{\partial(\mathcal{F}/T)}{\partial T}\right)_{\mathcal{V}} + \left(\frac{\partial(\mathcal{F}/T)}{\partial \mathcal{V}}\right)_T \left(\frac{\partial \mathcal{V}}{\partial T}\right)_V\right) \\
&= \delta\chi\left((E_r - E_s) - T^2\left(\left(\frac{\partial(F_r/T)}{\partial V_r}\right)_T \left(\frac{\partial V_r}{\partial T}\right)_V - \left(\frac{\partial(F_s/T)}{\partial V_s}\right)_T \left(\frac{\partial V_s}{\partial T}\right)_V\right)\right) \\
&\qquad + \left(\mathcal{E} - T^2\left(\frac{\partial(\mathcal{F}/T)}{\partial \mathcal{V}}\right)_T \left(\frac{\partial \mathcal{V}}{\partial T}\right)_V\right) \\
&= \sum x_j E_j + \delta\chi T\left(P_r\left(\frac{\partial V_r}{\partial T}\right)_V - P_s\left(\frac{\partial V_s}{\partial T}\right)_V\right) + T\mathcal{P}\left(\frac{\partial \mathcal{V}}{\partial T}\right)_V \\
&= \sum x_j E_j + \delta\chi T\left(P_r\left(\frac{\partial V_r}{\partial T}\right)_V - P_s\left(\frac{\partial V_s}{\partial T}\right)_V\right) + T\mathcal{P}\left(\frac{\partial}{\partial T}(V - \delta\chi(V_r - V_s))\right)_V \\
&= \sum x_j E_j + \delta\chi T\left((P_r - \mathcal{P})\left(\frac{\partial V_r}{\partial T}\right)_V - (P_s - \mathcal{P})\left(\frac{\partial V_s}{\partial T}\right)_V\right) \qquad (16)
\end{aligned}$$

Then, it suffices to show that

$$(P_r - \mathcal{P})\left(\frac{\partial V_r}{\partial T}\right)_V = (P_s - \mathcal{P})\left(\frac{\partial V_s}{\partial T}\right)_V \qquad (17)$$

However, this result must hold true for all pairs of indices (r, s) that we decide to shift from our starting point $(\chi_1, \chi_2, \chi_3, \ldots)$ and thus, $(P_j - \mathcal{P})\left(\frac{\partial V_j}{\partial T}\right)_V$ must be constant with respect to index j. Given c pure substances, consider some imaginary pure substance with $V^*(T, P_{base}), F^*\left(T, \frac{M^*}{V^*}\right)$ such that the resulting $P^* = -\left(\frac{\partial F^*}{\partial V^*}\right)_T$ satisfies

$$P^* = \frac{1}{\sum \frac{x_j V_j}{B_j}} \cdot \sum\left(\frac{x_j V_j}{B_j}\right) P_j \qquad (18)$$

It then follows that the pressure of a mixture of the original c pure substance and this original substance will always equal P^*. Thus, choosing this imaginary substance as index s in such a mixture of $c+1$ substances will require $(P_r - \mathcal{P})\left(\frac{\partial V_r}{\partial T}\right)_V = 0$. However since P_r is not necessarily equal to $\mathcal{P}$, we get $\left(\frac{\partial V_r}{\partial T}\right)_V = 0$ which is also not necessarily true.

§3 Counterexample

At this point I'm rather convinced that this is not actually true. We can note that both attempts at proving $E = \sum x_j E_j$ require $\left(\frac{\partial V}{\partial T}\right)_{V_c} = 0$, $P_c = P$, or some other equivalent to be true. Additionally the inductive step should work regardless of which pure substance we use in conjunction with the induction hypothesis so $\left(\frac{\partial V}{\partial T}\right)_{V_j} = 0$ should hold for all j. This of course is only true if all V_j are proportional, that is, $\frac{V_i(T, P_{base})}{V_j(T, P_{base})} = \mathcal{C}_{i,j}$ for some constant $\mathcal{C}_{i,j}$ for all indices $1 \leq i, j \leq c$. Thus in theory, it should be simple to construct such a counterexample.

Consider the simple case of $c = 2$, $V_1 = k_1 T^2 P_{base}$ and $V_2 = k_2 T^3 P_{base}^2$ for some constants k_1, k_2. For simplicity, suppose that they are separate. Note the bulk moduli $B_1 = -V_1 \left(\frac{\partial P_{base}}{\partial V_1}\right)_T = -P_{base}$ and $B_2 = -V_2 \left(\frac{\partial P_{base}}{\partial V_2}\right)_T = -\frac{P_{base}}{2}$. As of right now, we won't even bother to set F_1, F_2 and x_1, x_2. Then, we get

$$
\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_T \\
&= -x_1 \left(\frac{\partial F_1}{\partial V_1}\right)_T \left(\frac{\partial V_1}{\partial P_{base}}\right)_T \left(\frac{\partial P_{base}}{\partial V}\right)_T - x_2 \left(\frac{\partial F_2}{\partial V_2}\right)_T \left(\frac{\partial V_2}{\partial P_{base}}\right)_T \left(\frac{\partial P_{base}}{\partial V}\right)_T \\
&= \left(\frac{\partial P_{base}}{\partial V}\right)_T \left(x_1 P_1 \left(k_1 T^2\right) + x_2 P_2 \left(2k_2 T^3 P_{base}\right)\right) \\
&= \frac{\left(x_1 P_1 \left(k_1 T^2\right) + x_2 P_2 \left(2k_2 T^3 P_{base}\right)\right)}{x_1 \left(\frac{\partial V_1}{\partial P_{base}}\right)_T + x_2 \left(\frac{\partial V_2}{\partial P_{base}}\right)} \\
&= \frac{\left(x_1 P_1 \left(k_1 T^2\right) + x_2 P_2 \left(2k_2 T^3 P_{base}\right)\right)}{x_1 \left(k_1 T^2\right) + x_2 \left(2k_2 T^3 P_{base}\right)} \\
&= \frac{\left(\frac{x_1 V_1}{B_1}\right) P_1 + \left(\frac{x_2 V_2}{B_2}\right) P_2}{\frac{x_1 V_1}{B_1} + \frac{x_2 V_2}{B_2}}
\end{aligned}
\tag{19}
$$

and

$$
\begin{aligned}
E &= -T^2 \left(\frac{\partial (F/T)}{\partial T}\right)_V \\
&= -T^2 \left(x_1 \left(\frac{\partial (F_1/T)}{\partial T}\right)_V + x_2 \left(\frac{\partial (F_2/T)}{\partial T}\right)_V\right) \\
&= -x_1 T^2 \left(\left(\frac{\partial (F_1/T)}{\partial T}\right)_{V_1} + \left(\frac{\partial (F_1/T)}{\partial V_1}\right)_T \left(\left(\frac{\partial V_1}{\partial T}\right)_{P_{base}} + \left(\frac{\partial V_1}{\partial P_{base}}\right)_T \left(\frac{\partial P_{base}}{\partial T}\right)_V\right)\right) \\
&\quad - x_2 T^2 \left(\left(\frac{\partial (F_2/T)}{\partial T}\right)_{V_2} + \left(\frac{\partial (F_2/T)}{\partial V_2}\right)_T \left(\left(\frac{\partial V_2}{\partial T}\right)_{P_{base}} + \left(\frac{\partial V_2}{\partial P_{base}}\right)_T \left(\frac{\partial P_{base}}{\partial T}\right)_V\right)\right) \\
&= x_1 \left(E_1 - k_1 T \left(\frac{\partial F_1}{\partial V_1}\right)_T \left(2T P_{base} + T^2 \left(\frac{\partial P_{base}}{\partial T}\right)_V\right)\right) \\
&\quad + x_2 \left(E_2 - k_2 T \left(\frac{\partial F_2}{\partial V_2}\right)_T \left(3T^2 P_{base}^2 + 2T^3 P_{base} \left(\frac{\partial P_{base}}{\partial T}\right)_V\right)\right) \\
&= (x_1 E_1 + x_2 E_2) - x_1 P_1 k_1 T \left(2T P_{base} + T^2 \left(\frac{\partial P_{base}}{\partial T}\right)_V\right) - x_2 P_2 k_2 T \left(3T^2 P_{base}^2 + 2T^3 P_{base} \left(\frac{\partial P_{base}}{\partial T}\right)_V\right) \\
&= (x_1 E_1 + x_2 E_2) - T^2 P_{base} \left(2x_1 P_1 k_1 + 3x_2 P_2 k_2 T P_{base}\right) - T^3 \left(x_1 P_1 k_1 + 2x_2 P_2 k_2 T P_{base}\right) \left(\frac{\partial P_{base}}{\partial T}\right)_V \\
&= (x_1 E_1 + x_2 E_2) - T^2 P_{base} \left(2x_1 P_1 k_1 + 3x_2 P_2 k_2 T P_{base}\right) \\
&\quad + T^3 \left(x_1 P_1 k_1 + 2x_2 P_2 k_2 T P_{base}\right) \cdot \frac{2k_1 T P_{base} + 3k_2 T^2 P_{base}^2}{k_1 T^2 + 2k_2 T^3 P_{base}}
\end{aligned}
$$

$$= (x_1E_1 + x_2E_2) \\ - T^2P_{base}\left((2x_1P_1k_1 + 3x_2P_2k_2TP_{base}) - (x_1P_1k_1 + 2x_2P_2k_2TP_{base}) \cdot \frac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}}\right) \tag{20}$$

It then suffices to show that

$$(2x_1P_1k_1 + 3x_2P_2k_2TP_{base}) = (x_1P_1k_1 + 2x_2P_2k_2TP_{base}) \cdot \frac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}} \tag{21}$$

Since F_1, F_2 can be any function, P_1, P_2 can be considered as free variables so we need

$$\begin{cases} 2x_1P_1k_1 = x_1P_1k_1 \cdot \dfrac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}} \\ \\ 3x_2P_1k_2TP_{base} = 2x_2P_2k_2TP_{base} \cdot \dfrac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}} \end{cases} \tag{22}$$

$$\Rightarrow \begin{cases} \dfrac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}} = 2 \\ \\ \dfrac{2k_1 + 3k_2TP_{base}}{k_1 + 2k_2TP_{base}} = \dfrac{3}{2} \end{cases} \tag{23}$$

which is clearly impossible given x_1, k_1, x_2, k_2 are all nonzero.

§4 Counterproof

We can prove that the property $E = x_jE_j$ is true if and only if it holds for $c = 2$. The only if clause is obvious, since if the property does not hold for $c = 2$, it is not always true. Now, suppose the property holds for $c = 2$. This can be proven by reverse binary splitting.

Consider two sets of substances with Helmholtz energies $\{F_{1,1}, F_{1,2}, \ldots, F_{1,j}, \ldots\}$ and $\{F_{2,1}, F_{2,2}, \ldots, F_{2,k}, \ldots\}$ and volumes $\{V_{1,1}, V_{1,2}, \ldots, V_{1,j}, \ldots\}$ and $\{V_{2,1}, V_{2,2}, \ldots, V_{2,k}, \ldots\}$. Then, suppose the two sets of substances have internal ratios (ratios among the sets) $\{x_{1,1}, x_{1,2}, \ldots, x_{1,j}, \ldots\}$ and $\{x_{2,1}, x_{2,2}, \ldots, x_{2,k}, \ldots\}$. Then, we get the combined Helmholtz energies and volumes

$$\begin{cases} F_1 = \sum x_{1,j}F_{1,j} + \mathcal{C}T \\ \\ F_2 = \sum x_{2,k}F_{2,k} + \mathcal{C}T \end{cases} \tag{24}$$

$$\begin{cases} V_1 = \sum x_{1,j}V_{1,j} \\ \\ V_2 = \sum x_{2,k}V_{2,k} \end{cases} \tag{25}$$

Then, we want to show that we can combine the two mixtures as two pure substances in the ratios x_1, x_2 where $x_1 + x_2 = 1$ and still get the same result. Then, we get

$$\begin{aligned} F &= x_1F_1 + x_2F_2 + \mathcal{C}T \\ &= x_1 \sum x_{1,j}F_{1,j} + x_2 \sum x_{2,k}F_{2,k} + \mathcal{C}T \\ &= \sum (x_1x_{1,j})F_{1,j} + \sum (x_2x_{2,k})F_{2,k} + \mathcal{C}T \end{aligned} \tag{26}$$

and

$$\begin{aligned} V &= x_1V_1 + x_2V_2 \\ &= x_1\sum x_{1,j}V_{1,j} + x_2\sum x_{2,k}V_{2,k} \\ &= \sum(x_1x_{1,j})V_{1,j} + \sum(x_2x_{2,k})F_{2,k} \end{aligned} \tag{27}$$

as desired. Since P and E are derivable from F, V, the pressure and free energy from combining the two mixtures will follow similarly to a combination of two pure substances. Thus if the property holds for two substances or $c = 2$, we can perform binary splitting on each of the two submixtures until we obtain "mixtures" of size 2 or 1, both of which should hold. Thus, we have proven that the property holds for all c if and only if it holds for $c = 2$. Now, consider the equation

$$\begin{aligned} E &= \sum x_jE_j + T\sum x_j(P_j - P)\left(\frac{\partial V_j}{\partial T}\right)_{P_j} \\ &= (x_1E_1 + x_2E_2) + T\left(x_1(P_1 - P)\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2(P_2 - P)\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\right) \end{aligned} \tag{28}$$

Then we want to show that

$$x_1(P_1 - P)\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2(P_2 - P)\left(\frac{\partial V_2}{\partial T}\right)_{P_2} = 0 \tag{29}$$

Manipulating, we get

$$\begin{aligned}
& x_1(P_1 - P)\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2(P_2 - P)\left(\frac{\partial V_2}{\partial T}\right)_{P_2} = 0 \\
\Rightarrow\ & x_1P_1\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2P_2\left(\frac{\partial V_2}{\partial T}\right)_{P_2} = P\left(x_1\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\right) \\
\Rightarrow\ & \left(x_1P_1\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2P_2\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\right)\left(x_1\left(\frac{\partial V_1}{\partial P_1}\right)_T + x_2\left(\frac{\partial V_2}{\partial P_2}\right)_T\right) \\
& \quad = \left(\left(x_1\left(\frac{\partial V_1}{\partial T}\right)_{P_1} + x_2\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\right)\right)\left(x_1\left(\frac{\partial V_1}{\partial P_1}\right)_T P_1 + x_2\left(\frac{\partial V_2}{\partial P_2}\right)_T P_2\right) \\
\Rightarrow\ & P_1\left(\frac{\partial V_1}{\partial T}\right)_{P_1}\left(\frac{\partial V_2}{\partial P_2}\right)_T + P_2\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\left(\frac{\partial V_1}{\partial P_1}\right)_T = P_2\left(\frac{\partial V_1}{\partial T}\right)_{P_1}\left(\frac{\partial V_2}{\partial P_2}\right)_T + P_1\left(\frac{\partial V_2}{\partial T}\right)_{P_2}\left(\frac{\partial V_1}{\partial P_1}\right)_T \\
\Rightarrow\ & (P_1 - P_2)\left(\left(\frac{\partial V_1}{\partial T}\right)_{P_1}\left(\frac{\partial V_2}{\partial P_2}\right)_T - \left(\frac{\partial V_2}{\partial T}\right)_{P_2}\left(\frac{\partial V_1}{\partial P_1}\right)_T\right) = 0 \\
\Rightarrow\ & \left(\frac{\partial V_1}{\partial T}\right)_{P_1}\left(\frac{\partial V_2}{\partial P_2}\right)_T = \left(\frac{\partial V_2}{\partial T}\right)_{P_2}\left(\frac{\partial V_1}{\partial P_1}\right)_T \\
\Rightarrow\ & \left(\frac{\partial P_1}{\partial V_1}\right)_T\left(\frac{\partial V_1}{\partial T}\right)_{P_1} = \left(\frac{\partial P_2}{\partial V_2}\right)_T\left(\frac{\partial V_2}{\partial T}\right)_{P_2} \\
\Rightarrow\ & \left(\frac{\partial P_1}{\partial T}\right)_{V_1} = \left(\frac{\partial P_2}{\partial T}\right)_{V_2} \\
\Rightarrow\ & \left(\frac{\partial P_{base}}{\partial T}\right)_{V_1} = \left(\frac{\partial P_{base}}{\partial T}\right)_{V_2}
\end{aligned}$$

However, this is true if and only if $\dfrac{V_1}{V_2}$ is constant.

§5 Closed Form

Since the $\left(\frac{\partial P_j}{\partial T}\right)_{V_j}$ and $\left(\frac{\partial V_j}{\partial T}\right)_{P_j}$ terms keep persisting, we might get some insight by trying to convert it to some other derivative. Allow $\mathcal{E} = \sum x_j E_j$. Note that we can use Clairaut's after reverting P_j to $-\left(\frac{\partial F_j}{\partial V_j}\right)_T$, then continuing

$$\begin{aligned}\left(\frac{\partial P_j}{\partial T}\right)_{V_j} &= -\left(\frac{\partial}{\partial T}\left(\frac{\partial F_j}{\partial V_j}\right)_T\right)_{V_j} \\ &= -\left(\frac{\partial}{\partial V_j}\left(\frac{\partial F_j}{\partial T}\right)_{V_j}\right)_T \\ &= -\left(\frac{\partial}{\partial V_j}\left(\frac{F_j}{T} + T\left(\frac{\partial (F_j/T)}{\partial T}\right)_{V_j}\right)\right) \\ &= -\frac{1}{T}\left(\frac{\partial}{\partial V_j}(F_j - E_j)\right)_T \\ &= \frac{1}{T}\left(P_j + \left(\frac{\partial E_j}{\partial V_j}\right)_T\right) \end{aligned} \tag{30}$$

For $\left(\frac{\partial V_j}{\partial T}\right)_{P_j}$ we get

$$\left(\frac{\partial V_j}{\partial T}\right)_{P_j} = -\left(\frac{\partial V_j}{\partial P_j}\right)_T \left(\frac{\partial P_j}{\partial T}\right)_{V_j} = \frac{1}{T}\frac{V_j}{B_j}\left(P_j + \left(\frac{\partial E_j}{\partial V_j}\right)_T\right) \tag{31}$$

Then substituting into

$$E = \mathcal{E} + T\sum x_j (P_j - P)\left(\frac{\partial V_j}{\partial T}\right)_{P_j} \tag{32}$$

we get

$$\begin{aligned} E &= \mathcal{E} + T\sum x_j (P_j - P)\left(\frac{\partial V_j}{\partial T}\right)_{P_j} \\ &= \mathcal{E} + T\sum x_j (P_j - P)\cdot\frac{1}{T}\frac{V_j}{B_j}\left(P + \left(\frac{\partial E_j}{\partial V_j}\right)_T\right) \\ &= \mathcal{E} + \sum \frac{x_j V_j}{B_j}(P_j - P)\left(P_j + \left(\frac{\partial E_j}{\partial V_j}\right)_T\right) \end{aligned}$$

$\frac{\partial B}{\partial P} = \frac{B}{P} + P\frac{\partial (B/P)}{\partial P}$