Heat Capacities: Isochoric: Liquid Mixtures: Ideal

For an ideal binary liquid mixture the molar isobaric heat capacity is given by the mole fraction weighted sum of the isobaric heat capacities of the pure liquid components.

$$C_{pm}^{\text{mix};\text{id}} = x_1 \cdot C_{p_1}^{*} (\ell) + x_2 \cdot C_{p_2}^{*} (\ell) \quad (a)$$

Both $C_{p_1}^{*} (\ell)$ and $C_{p_2}^{*} (\ell)$ can be measured so that $C_{pm}^{\text{mix};\text{id}}$ can be calculated for a given mixture as a function of mole fraction composition.

Further $\Delta_{\text{mix}} C_{p}^{\text{id}} (\text{id}) = 0 \quad (b)$

The isochoric heat capacity of the corresponding ideal mixture is related to the isobaric heat capacity using equation (c) [1].

$$C_{Vm}^{\text{mix};\text{id}} = C_{pm}^{\text{mix};\text{id}} - \frac{T \cdot [E_{pm}^{\text{mix};\text{id}}]^2}{K_{Tm}^{\text{mix};\text{id}}} \quad (c)$$

Equations (a) and (c) provide an equation for $C_{Vm}^{\text{mix};\text{id}}$ in terms of the isochoric heat capacities of the pure liquid components.

$$C_{Vm}^{\text{mix};\text{id}} =
\begin{align*}
x_1 \cdot \left[ C_{V_1}^{*} (\ell) + \frac{T \cdot [E_{p_1}^{*} (\ell)]^2}{K_{T_1}^{*} (\ell)} \right] &+ x_2 \cdot \left[ C_{V_2}^{*} (\ell) + \frac{T \cdot [E_{p_2}^{*} (\ell)]^2}{K_{T_2}^{*} (\ell)} \right] \\
&\quad - \frac{T \cdot [E_{pm}^{\text{mix};\text{id}}]^2}{K_{Tm}^{\text{mix};\text{id}}} \quad (d)
\end{align*}$$

In terms of forming an ideal binary liquid mixture from two pure components,

$$\Delta_{\text{mix}} C_{Vm}^{\text{id}} = x_1 \cdot \left[ \frac{T \cdot [E_{p_1}^{*} (\ell)]^2}{K_{T_1}^{*} (\ell)} \right] + x_2 \cdot \left[ \frac{T \cdot [E_{p_2}^{*} (\ell)]^2}{K_{T_2}^{*} (\ell)} \right] \quad (e)$$

The equations become more complicated as we switch conditions from the intensive variables, $T$ and $p$, to extensive variables such as entropy and volume. The equations become even more complicated when we turn to a description of real mixtures.
Footnote

[1] Consider a closed system subjected to a change in temperature, the system remaining at equilibrium where the affinity for spontaneous change is zero.

Then
\[ C_p(A = 0) = \left( \frac{\partial H}{\partial T} \right)_{p,A=0} \quad \text{and} \quad C_V(A = 0) = \left( \frac{\partial U}{\partial T} \right)_{V,A=0} \]

In the following we drop the condition ‘A=0’ and take it as implicit in the following analysis. [A similar set of equations can be written for the condition ‘at fixed ξ’.

Then
\[ C_p - C_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V \]

but by definition, \( H = U + p \cdot V \)

Then
\[ C_p - C_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial H}{\partial T} \right)_V + \nabla \cdot \left( \frac{\partial p}{\partial T} \right)_V \]

Using a calculus operation, \( \left( \frac{\partial H}{\partial T} \right)_V = \left( \frac{\partial H}{\partial T} \right)_p + \nabla \cdot \left( \frac{\partial p}{\partial T} \right)_T \)

Then, \( C_p - C_V = \left[ V - \left( \frac{\partial H}{\partial T} \right)_T \right] \cdot \left( \frac{\partial p}{\partial T} \right)_V \)

By definition \( H = G + T \cdot S \); then \( \frac{\partial H}{\partial p} = \frac{\partial G}{\partial p} + T \cdot \frac{\partial S}{\partial p} \)

A Maxwell equation requires that \( \frac{\partial S}{\partial p} = -\frac{\partial V}{\partial T} \)

Then, \( \frac{\partial H}{\partial p} = V - T \cdot \left( \frac{\partial V}{\partial T} \right)_p \)

Hence, \( C_p - C_V = T \cdot \left( \frac{\partial V}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial T} \right)_V \)

A calculus operation requires that
\[ \left( \frac{\partial p}{\partial T} \right)_V \cdot \left( \frac{\partial T}{\partial V} \right)_p \cdot \left( \frac{\partial V}{\partial p} \right)_T = -1 \]

Then \( C_p - C_V = -T \cdot \left[ \left( \frac{\partial V}{\partial T} \right)_p \right]^2 \cdot \left[ \left( \frac{\partial V}{\partial p} \right)_T \right]^{-1} \)