An aqueous solution is prepared using $n_1$ moles of water (\(\ell\)) and $n_j$ moles of solute at temperature $T$ and pressure $p$. The system is at equilibrium where the affinity for spontaneous change is zero.

Hence,

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

Heat capacities describe a pathway. There are two limiting pathways. The system can be displaced either to a nearby state along a pathway for which $\xi$ is constant or along a pathway for which the affinity for spontaneous change is constant. The accompanying differential changes in enthalpies are unlikely to be the same. In fact they are related using a calculus procedure.

$$\left(\frac{\partial H}{\partial T}\right)_{A, p} = \left(\frac{\partial H}{\partial T}\right)_{\xi, p} - \left(\frac{\partial A}{\partial T}\right)_{\xi, p} \cdot \left(\frac{\partial \xi}{\partial A}\right)_{T, p} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T, p} \quad (b)$$

If the original state was an equilibrium state we write this equation in the following form which incorporates an equation for the dependence of affinity $A$ on temperature at equilibrium.

$$\left(\frac{\partial H}{\partial T}\right)_{A=0, p} = \left(\frac{\partial H}{\partial T}\right)_{\xi^{\text{eq}}, p} - \frac{1}{T} \left[\left(\frac{\partial H}{\partial \xi}\right)_{T, p}^{\text{eq}}\right]^2 \cdot \left(\frac{\partial \xi}{\partial A}\right)_{T, p}^{\text{eq}} \quad (c)$$

Then from the definition of isobaric heat capacity [1],

$$C_p(A = 0) = C_p\left(\xi^{\text{eq}}\right) - \frac{1}{T} \left[\left(\frac{\partial H}{\partial \xi}\right)_{T, p}^{\text{eq}}\right]^2 \cdot \left(\frac{\partial \xi}{\partial A}\right)_{T, p}^{\text{eq}} \quad (d)$$

Here $(\partial H/\partial \xi)_{T, p}^{\text{eq}}$ is the enthalpy of reaction. For a stable equilibrium state $(\partial A/\partial \xi)_{T, p}^{\text{eq}}$ is negative.

Hence,

$$C_p(A = 0) > C_p\left(\xi^{\text{eq}}\right) \quad (e)$$

Here $C_p(A = 0)$ is the equilibrium heat capacity signalling that when heat $q$ passes into the system the composition/organisation of the system changes in order that the Gibbs energy of the system remains at
a minimum. In contrast $C_p(\xi^{eq})$ is the frozen capacity signalling that no changes occur in the composition/organisation in the system such that the Gibbs energy of the system is displaced from the original minimum. Moreover, equation (e) shows that the equilibrium isobaric heat capacity is always larger than the frozen isobaric heat capacity. Indeed we can often treat the extensive equilibrium property $C_p(A = 0)$ as a function of state (although it is not).

**Footnote**

\[ [1] \quad \frac{1}{T} \cdot \left[ \left( \frac{\partial H}{\partial \xi} \right)_{T,p}^{eq} \right]^2 \cdot \left( \frac{\partial \xi}{\partial A} \right)_{T,p} = \frac{1}{[K]} \cdot \left[ \frac{J}{mol} \right]^2 \cdot \left[ \frac{mol}{J \cdot mol^1} \right] = [J \cdot K^{-1}] \]