Cold Denaturation

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Starting equations.

$$\Delta H = \Delta H^0 + \Delta C_P (T - T_0) \tag{1a}$$
$$\Delta S = \Delta S^0 + \Delta C_P \ln \frac{T}{T_0} \tag{1b}$$

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

We put equations 1a and 1b into equation 2 and we get the following.

$$\Delta G = \Delta H^0 + \Delta C_P (T - T_0) - T \times \left(\Delta S^0 + \Delta C_P \ln \frac{T}{T_0} \right) \tag{3}$$
$$= \left(\Delta H^0 - T\Delta S^0 \right) + \Delta C_P (T - T_0) - T\Delta C_P \ln \frac{T}{T_0} \tag{4}$$

where T_0 is any reference temperature.

Equation 4 at T_g and T_g'

At temperature Tg and T_g' ΔG in equations 2 goes to 0

$$\Delta H(T_g) = T_g \Delta S(T_g) \tag{5a}$$
$$\Delta H(T_g') = T_g' \Delta S(T_g') \tag{5b}$$

In equation 4, we choose reference temperature are T_g and compute ΔG at T_g' which is 0.

$$0 = \Delta G(T_g') = \Delta H(T_g) - T_g' \Delta S(T_g) + \Delta C_P (T_g' - T_g) - T_g' \Delta C_P \ln \frac{T_g'}{T_g} \tag{6}$$
$$= \Delta H(T_g) - T_g' \frac{\Delta H(T_g)}{T_g} + \Delta C_P (T_g' - T_g) - T_g' \Delta C_P \ln \frac{T_g'}{T_g} \qquad \text{substituting 5a} \tag{7}$$
$$= \Delta H(T_g) \left(1 - \frac{T_g'}{T_g} \right) + \Delta C_P (T_g' - T_g) - T_g' \Delta C_P \ln \frac{T_g'}{T_g} \tag{8}$$
$$= \Delta H(T_g) \left(\frac{T_g - T_g'}{T_g} \right) + \Delta C_P (T_g' - T_g) - T_g' \Delta C_P \ln \frac{T_g'}{T_g} \tag{9}$$
$$\tag{10}$$

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$\Longrightarrow$

$$-\frac{\Delta H(T_g)}{\Delta C_P}\left(\frac{T_g - T_g'}{T_g}\right) = T_g' - T_g - T_g' \ln \frac{T_g'}{T_g} \tag{11}$$

$$= T_g' - T_g + T_g' \ln \frac{T_g}{T_g'} \tag{12}$$

$$= T_g' - T_g + T_g' \ln \left(1 + \frac{T_g - T_g'}{T_g'}\right) \qquad x = 1 + x - 1 \tag{13}$$

$$= T_g' - T_g + T_g' \left(\frac{T_g - T_g'}{T_g'} - \frac{1}{2}\left(\frac{T_g - T_g'}{T_g'}\right)^2\right) \qquad \ln(1+x) = x - \tfrac{x^2}{2} \ldots \tag{14}$$

$$= T_g' - T_g + T_g - T_g' - \frac{T_g'}{2}\left(\frac{T_g - T_g'}{T_g'}\right)^2 \tag{15}$$

$$\Longrightarrow -\frac{\Delta H(T_g)}{\Delta C_P}\left(\frac{T_g - T_g'}{T_g}\right) = -\frac{T_g'}{2}\left(\frac{T_g - T_g'}{T_g'}\right)^2 \tag{16}$$

$$\frac{\Delta H(T_g)}{\Delta C_P} = \frac{T_g' T_g}{2}\left(\frac{T_g - T_g'}{T_g'}\right)^2 \tag{17}$$

$$\frac{2\Delta H(T_g)}{\Delta C_P} = T_g \frac{T_g - T_g'}{T_g'} \tag{18}$$

$$\frac{2\Delta H(T_g)}{\Delta C_P} = \frac{T_g^2}{T_g'} - T_g \tag{19}$$

$$\frac{2\Delta H(T_g)}{\Delta C_P} + T_g = \frac{T_g^2}{T_g'} \tag{20}$$

$$\boxed{T_g' = \frac{T_g^2}{\frac{2\Delta H(T_g)}{\Delta C_P} + T_g}} \tag{21}$$