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Course 565/665 Lecturer prof. Cavagnero

Day 4.13.04 Date 9:55 am

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we know: $\mu = \mu^\circ + kT\ln p$

$dG = \mu\, dN$ at const. T. P. $\quad kN = R$.

then $G = G^\circ + RT\ln p$

For unfolding process:

$$\Delta G = \Delta G^\circ + RT\ln\frac{P_u}{P_N} = \Delta G^\circ + RT\ln K_{P_{NU}} \quad \cdots (I)$$

In the condensed phase: $\underset{\text{activity}}{a} = \overset{\text{activity coefficient}}{\gamma}\underset{\text{mole fraction}}{X}$

for ideal solution: $\gamma = 1 \Rightarrow a \approx X$.

update eqn (I) for condensed phase:

$$\Delta G = \Delta G^\circ + RT\ln K_{NU} \qquad K_{NU} = \frac{a_u}{a_N}$$

at equilibrium: $\Delta G = 0$. $\quad \Delta G = \Delta G^\circ + RT\ln K_{NU} = 0$

$$\Rightarrow \Delta G^\circ = -RT\ln K_{NU}$$

At certain T: $K_{NU} = \frac{a_u}{a_N} = 1$ ⇒ define this as melting T (T_m)

at T_m: $\Delta G^\circ_m + RT\ln 1 = 0$ $\quad \left\{ \begin{array}{l} \Delta G^\circ_m = 0 \\ \Delta G = 0 \end{array} \right.$

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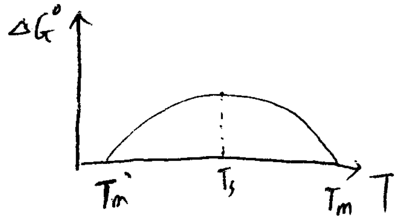
$\Delta H_m^\circ - T_m \Delta S_m^\circ = \Delta G_m^\circ = 0$ $\Delta H_m^\circ = T_m \Delta S_m^\circ$

therefore. $\Delta G^\circ = \Delta C_p (T - T_m) + \Delta H_m^\circ - T\left(\Delta C_p \ln\frac{T}{T_m} + \frac{\Delta H_m^\circ}{T_m}\right)$

rearrange: $\Delta G^\circ = \Delta H_m^\circ \left(1 - \frac{T}{T_m}\right) + \Delta C_p \left(T - T_m - T \ln\frac{T}{T_m}\right)$



T_m' : cold unfolding T.

In most cases, maximum ΔG° is at room T.

typically: T_m range over 60 - 90°C.

~~Recall~~. Note. $\left(\frac{\partial \Delta G_{NU}^\circ}{\partial T}\right)_p = -\Delta S_{NU}^\circ$

$T_s < T < T_m$. $\Delta S_{NU}^\circ > 0 \Rightarrow S_U > S_N$

$T_m' < T < T_s$: $\Delta S_{NU}^\circ < 0 \Rightarrow S_N > S_U$

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