

Secret Code : 20
Biophysical Chemistry PS5

5.1A) for $A \rightleftharpoons B$ @ 310 K

$$\Delta\bar{G}_{rxn}^\circ = M_B^\circ - M_A^\circ = -15 \text{ kJ/mol} - 1 \text{ kJ/mol} = \boxed{-14 \text{ kJ/mol}} = -14,000 \text{ J/mol}$$

5.1B) $K_{eq}?$ $\Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln(Q) = 0$

@ equilibrium

$$\Delta\bar{G}^\circ = -RT\ln(K_{eq})$$

$$K_{eq} = e^{-\frac{\Delta\bar{G}^\circ}{RT}} = e^{\frac{-14,000 \text{ J/mol}}{8.314 \times 310}} = \boxed{228.5}$$

5.1C) $\Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln(Q)$

$$Q = \frac{[B]}{[A]} = \frac{0.01 \text{ M}}{1.99 \text{ M}}$$

$$\Delta\bar{G} = -14,000 \text{ J} + (8.314 \text{ J/K}) (310) \ln(Q)$$

$$\Delta\bar{G} = \boxed{-27,643.47 \text{ J/mol}} = -27.6 \text{ kJ/mol}$$

5.1D) $n_T = n_A + n_B = 2 \text{ mol}$

$$2 - n_A = n_B$$

$$K_{eq} = 228.5 = \frac{[B]}{[A]}$$

$$228.5 = \frac{\frac{n_B}{1 \text{ L}}}{\frac{n_A}{1 \text{ L}}} = \frac{n_B}{n_A} = \frac{2 - n_A}{n_A} = \frac{2}{n_A} - 1$$

$$228.5 = \frac{2}{n_A}$$

$$n_A = \frac{2}{228.5} = 0.00871 \text{ mol}$$

$$n_B = 2 - n_A = 1.9913 \text{ mol}$$

$$[A]_{eq} = 0.00871 / 1 \text{ L} = \boxed{0.00871 \text{ M}}$$

$$[B]_{eq} = 1.9913 / 1 \text{ L} = \boxed{1.9913 \text{ M}}$$

5.1E)

$$\begin{aligned} G_T^\circ &= n_A M_A^\circ + n_B M_B^\circ \\ &= n_A (M_A^\circ + RT\ln[\frac{[A]_{eq}}{1 \text{ M}}]) + n_B (M_B^\circ + RT\ln[\frac{[B]_{eq}}{1 \text{ M}}]) \\ &= 2 \left(-1000 \frac{\text{J}}{\text{mol}} + RT\ln(\frac{1}{1 \text{ M}}) \right) + 1 \text{ mol} \left(-15,000 \frac{\text{J}}{\text{mol}} + RT\ln(\frac{1}{1 \text{ M}}) \right) \\ &= -1000 \text{ J} + -15,000 \text{ J} = \boxed{-16000 \text{ J}} \end{aligned}$$

$$\begin{aligned} @ \text{std St.} \quad n_A &= 2 \\ n_B &= 1 \\ [A] &= 1 \\ [B] &= 1 \\ n_A F &= 0.00871 \text{ mol} \\ n_B F &= 1.9913 \text{ mol} \end{aligned}$$

$$\begin{aligned} G_{T,F} &= (0.00871) (M_A^\circ + RT\ln(\frac{[A]_{eq}}{1 \text{ M}})) + (1.9913) (M_B^\circ + RT\ln(\frac{[B]_{eq}}{1 \text{ M}})) \\ &= (0.00871 \text{ mol}) (-1000 \frac{\text{J}}{\text{mol}} + 8.3145 \frac{\text{J}}{\text{mol K}} \cdot 310 \text{ K} \cdot \ln(\frac{0.00871 \text{ M}}{1 \text{ M}})) + (1.9913) \cdot (-15,000 \frac{\text{J}}{\text{mol}} + 8.3145 \frac{\text{J}}{\text{mol K}} \cdot 310 \text{ K} \cdot \ln(\frac{1.9913 \text{ M}}{1 \text{ M}})) \\ &= -26449.3 \text{ J} \end{aligned}$$

$$\Delta G_T = G_{T,F} - G_T^\circ = \boxed{-10,449.3 \text{ J}}$$

$$5.2A) \ln(\kappa) = -\frac{\Delta\bar{G}^\circ}{RT} = -\frac{(\Delta\bar{H}^\circ - T\Delta\bar{S}^\circ)}{RT} = -\frac{\Delta\bar{H}^\circ}{RT} + \frac{\Delta\bar{S}^\circ}{R}$$

5.2B) The + reaction endothermic because heat is added resulting in $H_F^\circ > H_I^\circ$

5.2C) The + reaction increasingly favors products as $T \uparrow$
while - reaction increasingly favors reactants.

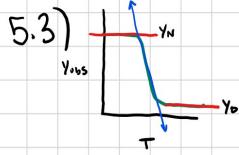
5.2D) They both approach $\ln(K_{eq})$ values of $\frac{\Delta\bar{S}^\circ}{R}$

$$\lim_{T \rightarrow 0} \ln(K_{eq}) = \lim_{T \rightarrow \infty} \left(-\frac{\Delta\bar{H}^\circ}{RT} + \frac{\Delta\bar{S}^\circ}{R} \right) = \frac{\Delta\bar{S}^\circ}{R}$$

5.2E) At low T, + approaches $-\infty$ and - approaches $+\infty$

$$\lim_{T \rightarrow 0} \left(-\frac{\Delta\bar{H}^\circ}{RT} + \frac{\Delta\bar{S}^\circ}{R} \right) = -\frac{\Delta\bar{H}^\circ}{R}(0) + \frac{\Delta\bar{S}^\circ}{R} = \text{Sign}(\Delta\bar{H}^\circ) \cdot -\infty$$

5.2F) See lab.



$$\Delta\bar{G}^\circ = -RT\ln(K_{eq}) = \Delta\bar{H}^\circ - \Delta\bar{S}^\circ$$

$$K_{eq} = e^{-\Delta\bar{G}^\circ/RT}$$

$$K_{eq} = e^{-(\Delta\bar{H}^\circ - T\Delta\bar{S}^\circ)/RT}$$

$$K_{eq} = e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}} = \frac{[N]}{[D]}$$



$$\begin{aligned} Y_{obs} &= f_N Y_N + f_D Y_D \\ &= \frac{[N]}{[N]+[D]} Y_N + \frac{[D]}{[N]+[D]} Y_D \\ &\Rightarrow = \frac{K_{eq}}{K_{eq}+1} Y_N + \frac{1}{K_{eq}+1} Y_D \quad (\frac{f_D}{f_N} = 1 - \frac{K_{eq}}{K_{eq}+1}) \\ &= \frac{K_{eq}}{K_{eq}+1} Y_N + (1 - \frac{K_{eq}}{K_{eq}+1}) Y_D \\ &= \frac{K_{eq}}{K_{eq}+1} (Y_N - Y_D) + Y_D \end{aligned}$$

Where Y_N is fluorescence observed @ folded baseline
 Y_D is fluorescence observed @ denatured baseline
 R is ideal gas const.
 ΔS° and ΔH° are known and
Temp. indep

$$Y_{obs} = Y_D + \frac{(Y_N - Y_D) e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}}}{1 + e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}}}$$

$$\begin{aligned} \frac{\partial Y_{obs}}{\partial T} &= \frac{1}{\partial T} Y_D + \frac{\frac{\partial}{\partial T} (Y_N - Y_D) e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}}}{1 + e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}}} \\ &= (Y_N - Y_D) \frac{\frac{\partial}{\partial T} \left(e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}} \right)}{1 + e^{\frac{(\Delta\bar{S}^\circ - \Delta\bar{H}^\circ)}{RT}}} \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} \frac{1}{e^{\frac{(\Delta\bar{H}^\circ/RT - \Delta\bar{S}^\circ/R)}{}} + 1} &= \frac{d}{dt} \left(\frac{1}{e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1} \right) = \frac{d}{dt} (e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1)^{-1} \\ &= -1(e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1)^{-2} \cdot (-\frac{1}{RT^2} \Delta\bar{H}^\circ) e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} \quad (\text{chain rule}) \end{aligned}$$

$$= \frac{e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}}}{(e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1)^2} \cdot \frac{\Delta\bar{H}^\circ}{RT^2}$$

$$= \left(\frac{1}{e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1} \right)^2 \frac{\Delta\bar{H}^\circ}{RT^2}$$

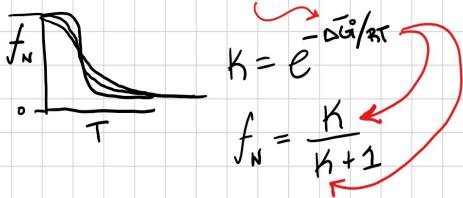
$$= \frac{1}{(\frac{1}{K} + 1)^2} \times \frac{\frac{K^2}{1}}{\frac{K^2}{1}} \Rightarrow \frac{K}{(K+1)^2}$$

$$= \frac{K}{(1+K)^2} \frac{\Delta\bar{H}^\circ}{RT^2}$$

$$\boxed{\frac{\partial Y_{obs}}{\partial T} = (Y_N - Y_D) \frac{K}{(1+K)^2} \frac{\Delta\bar{H}^\circ}{RT^2}}$$

5.4A) See lab.

5.4B)



$$\Delta\bar{G}^\circ = \Delta\bar{H}_{Tm} + \Delta\bar{C}_p(T-T_m) - T \cdot \frac{\Delta\bar{H}_{Tm}}{T_m} - T \Delta\bar{C}_p \ln\left(\frac{T}{T_m}\right)$$

$$K = e^{-\Delta G^\circ / RT}$$

$$f_N = \frac{K}{K+1}$$

N ⇌ D

$$\Delta\bar{G}^\circ = \Delta\bar{H} - T\Delta\bar{S}$$

$\Delta\bar{H}_{Tm}$ is @ $\Delta\bar{G}^\circ = 0$ equilibrium.

5.5A) See Jupyter

$$Y_N = aT + b$$

$$Y_D = cT + d$$

$$Y_{obs} = Y_D + \frac{(Y_N - Y_D)e^{\Delta\bar{H}^\circ(T-T_m)/RTT_m}}{1 + e^{\Delta\bar{H}^\circ(T-T_m)/RTT_m}}$$

$$\Delta\bar{H}^\circ \approx 400 \quad \text{because } \Delta T \sim 10 \text{ K}$$

5.5B) See Jupyter

$$5.5C) \Delta\bar{G}^\circ = \Delta\bar{H}_{Tm} + \Delta\bar{C}_p(T-T_m) - \frac{T\Delta\bar{H}_{Tm}}{T_m} - T\Delta\bar{C}_p \ln\left(\frac{T}{T_m}\right)$$

$$\Delta\bar{H}_{Tm} = -465.75 \text{ kJ/mol}$$

$$\Delta\bar{C}_p = -6.4 \text{ kJ/mol K}$$

$$T_m = 340.5 \text{ K}$$

$$= -465.75 + -6.4(350 - 340.5) - \frac{350 \cdot -465.75}{340.5} - 350 \cdot -6.4 \ln\left(\frac{350}{340.5}\right)$$

$$= 13.79 \text{ kJ/mol } @ 350 \text{ K}$$

$$\boxed{\text{Similarly } @ 310 \text{ K: } -32.72 \text{ kJ/mol}}$$

5.5D) Cold denaturation Temp: 214.326 K

(obtained by graphical analysis and check in .ipynb)