

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.

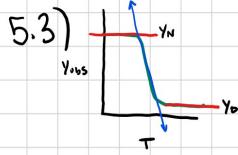
5.2D) They both approach $\ln(K_{eq})$ values of $\frac{\Delta\bar{S}^\circ}{R}$

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

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.

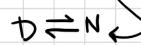


$$\Delta\bar{G}^\circ = -RT\ln(K_{eq}) = \Delta\bar{H}^\circ - \Delta\bar{S}^\circ$$

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

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

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



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

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

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

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

$$\begin{aligned} \frac{d}{dt} \frac{1}{e^{\frac{(\Delta\bar{H}^\circ/RT - \Delta\bar{S}^\circ/R)}{}} + 1} &= \frac{d}{dt} \left(\frac{1}{e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1} \right) = \frac{d}{dt} (e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1)^{-1} \\ &= -1(e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} + 1)^{-2} \cdot (-1 \frac{\Delta\bar{H}^\circ}{RT^2} + 0) e^{\frac{\Delta\bar{H}^\circ}{RT} - \frac{\Delta\bar{S}^\circ}{R}} \quad (\text{chain rule}) \end{aligned}$$

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

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

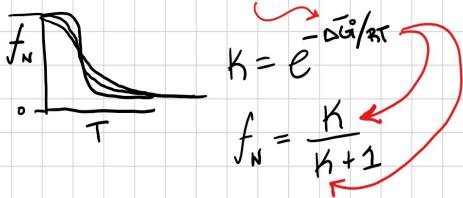
$$= \frac{1}{(\frac{1}{K} + 1)^2} \times \frac{\frac{K^2}{1}}{\frac{K^2}{1}} \Rightarrow \frac{K}{(K+1)^2}$$

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

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

5.4A) See lab.

5.4B)



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

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

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

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

$$Y_N = aT + b$$

$$Y_D = cT + d$$

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

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

5.5B) See Jupyter

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

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

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

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

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

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

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

5.5D) Cold denaturation Temp: 214.326 K

(obtained by graphical analysis and check in .ipynb)

problem_set_5

November 1, 2020

```
[1]: import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
import pandas as pd
```

0.0.1 Question 1

part A & B

```
[2]: muA = -1 #kJ/mol
muB = -15 #kJ/mol
dG_st = muB - muA #kJ/mol
dG_st *= 1000 #J / mol
R = 8.3145 #J/ mol K
T = 310 #K
Keq = np.e ** (-dG_st/(R*T))
print('deltaG Standard (Joules/mol): ', dG_st)
print('Keq: ', Keq)
```

deltaG Standard (Joules/mol): -14000
Keq: 228.5215058109785

Part C

```
[3]: B = 0.01 #mol/1L
A = 1.99 #mol/1L
Q = B/A

dG = dG_st + R*T*np.log(Q)
print('deltaG (Joules/mol): ', dG)
```

deltaG (Joules/mol): -27643.466719203258

Part D

```
[4]: n_tot = 2 #mol
L = 1 #Liters
nA = 2/(Keq + 1) #mol
nB = n_tot - nA #mol
M_A = nA/L
```

```
M_B = nB/L
print(f' [A] = {M_A:.4f} M and [B] = {M_B:.4f} M')
```

[A] = 0.0087 M and [B] = 1.9913 M

Part E

```
[5]: Gt_I = 1*muA*1000 + 1*muB*1000
Gt_F = nA*(muA*1000 + R*T*np.log(nA/1)) + nB*(muB*1000 + R*T*np.log(nB))

DGt = Gt_F - Gt_I
print(Gt_I)
print(Gt_F)
print(' ',DGt)
```

-16000
-26449.34201097052
-10449.342010970518

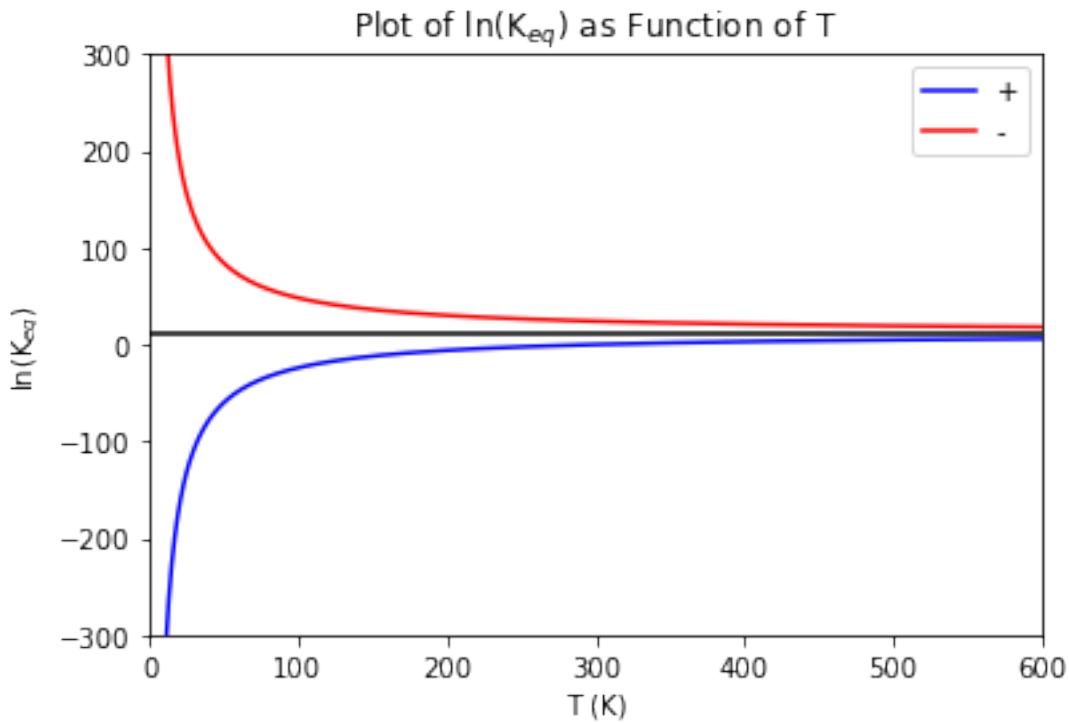
0.0.2 Question 2

Part A

```
[6]: DSst = 100 #J/K mol
def ln(T, DH_st, DS_st):
    R = 8.3145 #J/mol K
    return -DH_st/(R*T) + DS_st/R

X = np.arange(1, 601, 1)
positive = ln(X, 30000, DSst)
negative = ln(X, -30000, DSst)

plt.plot(X, positive, 'b', label="+")
plt.plot(X, negative, 'r', label="-")
plt.axis([0, 600, -300, 300])
plt.legend()
plt.xlabel("T (K)")
plt.ylabel("ln(K$_{eq})$")
plt.title("Plot of ln(K$_{eq})$ as Function of T")
plt.hlines(DSst/R, 0, 1000, 'k');
```



Part F

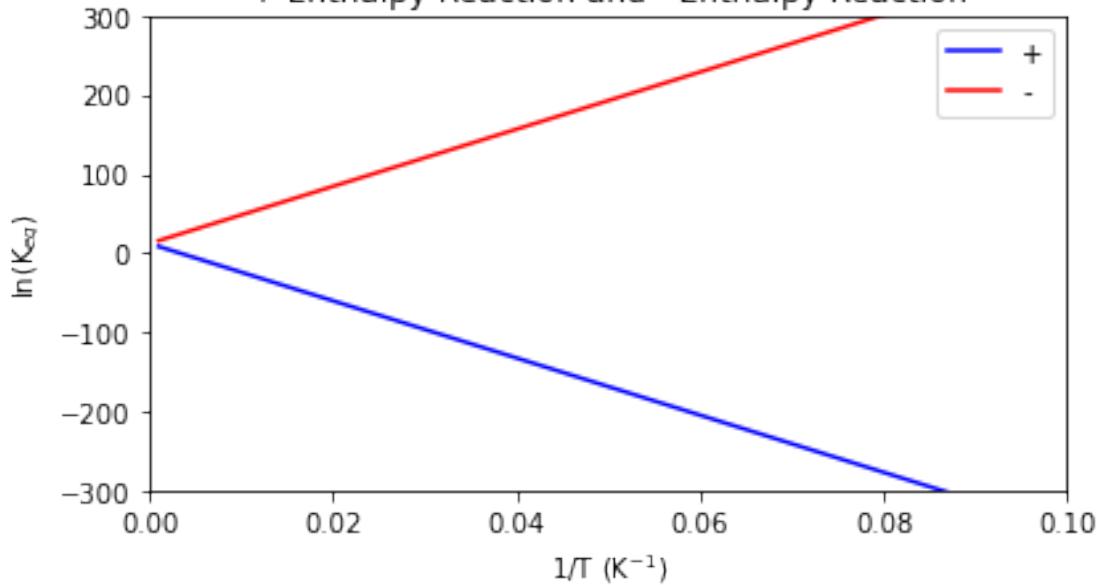
> The slope of the Van't Hoff plot is equal to $-\Delta H / R$ and thus is always linear. It is positive when ΔH is negative and negative when ΔH is positive.

```
[7]: Xs = np.arange(0.001, 0.1001, 0.001)
vh_Xs = np.array([1/x for x in Xs])

pos = ln(vh_Xs, 30000, DSst)
neg = ln(vh_Xs, -30000, DSst)

plt.plot(Xs, pos, "b", label="+")
plt.plot(Xs, neg, "r", label="-")
plt.legend()
plt.axis([0, 0.1, -300, 300])
plt.xlabel("1/T (K-1)")
plt.ylabel("ln(Keq)")
plt.title("Van't Hoff Plot Showing Dependence of \nln(Keq) on Inverse\u2192Temperature for + Enthalpy Reaction and - Enthalpy Reaction")
plt.tight_layout();
```

Van't Hoff Plot Showing Dependence of
 $\ln(K_{eq})$ on Inverse Temperature for
+ Enthalpy Reaction and - Enthalpy Reaction



0.0.3 Problem 5.4

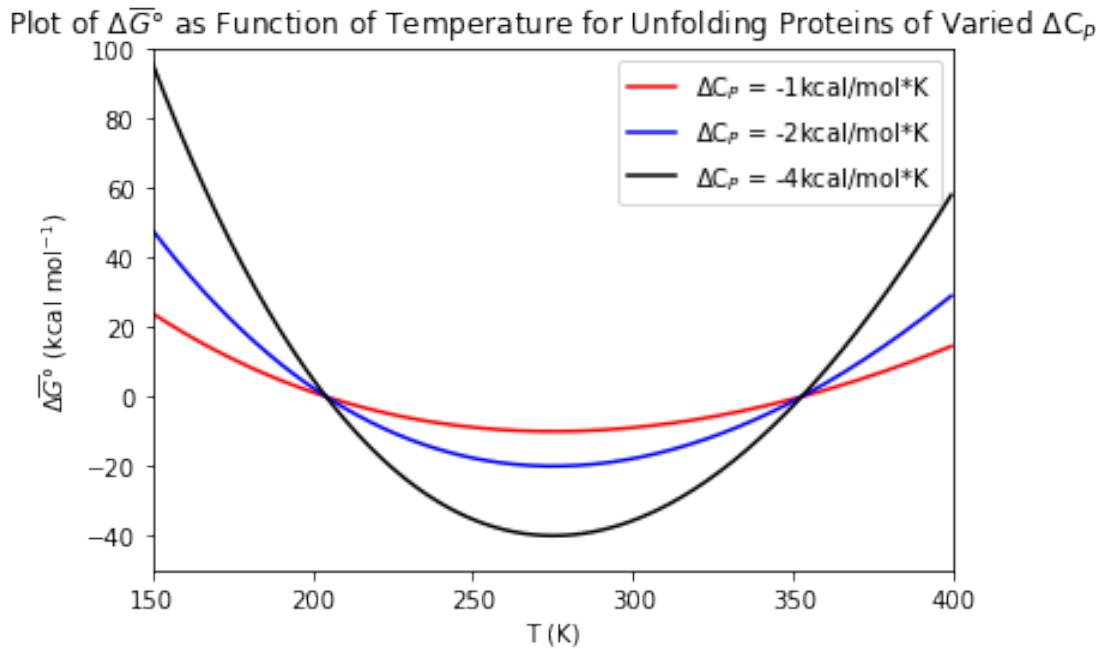
Part A

```
[8]: def DGbarstd(T, DCp, Th=265, Ts=275):
    return DCp*(T-Th) - T*DCp*np.log(T/Ts)

Ts = np.arange(150, 400, 1)
A = DGbarstd(Ts, -1)
B = DGbarstd(Ts, -2)
C = DGbarstd(Ts, -4)

plt.plot(Ts, A, 'r', label="$\Delta C_P = -1 \text{kcal/mol}\cdot\text{K}$")
plt.plot(Ts, B, 'b', label="$\Delta C_P = -2 \text{kcal/mol}\cdot\text{K}$")
plt.plot(Ts, C, 'k', label="$\Delta C_P = -4 \text{kcal/mol}\cdot\text{K}$")
plt.legend()
plt.axis([150, 400, -50, 100])
plt.xlabel("T (K)")
plt.title("Plot of $\overline{\Delta G}^\circ$ as Function of Temperature  

→for Unfolding Proteins of Varied $\Delta C_P$")
plt.ylabel("$\overline{\Delta G}^\circ (\text{kcal mol}^{-1})$");
```



Part B

> Protein F has the steepest transition because the slope of the transition is set by ΔH_{T_m} . According to equation 8.47 in the textbook, the first temperature derivative of the fraction native function is $\frac{K}{(1+K)^2} \frac{\Delta\bar{H}}{RT^2}$ and thus as the magnitude of ΔH_{T_m} increases, so does the steepness of the unfolding curve.

```
[9]: def fraction_native(T, Tm, DHtm, DCp):
    R = 1.987204e-3 #IDG constant in kcal/mol K
    DGb = DHtm + (DCp*(T-Tm)) - ((T*DHtm)/Tm) - (T*DCp*np.log(T/Tm))
    K = np.e ** ((-1*DGb)/(R*T))
    fn = K / (K+1)
    return fn

Ts = np.arange(300,500,0.01)
D = fraction_native(Ts, 330, -50, -2)
E = fraction_native(Ts, 330, -100, -2)
F = fraction_native(Ts, 330, -200, -2)

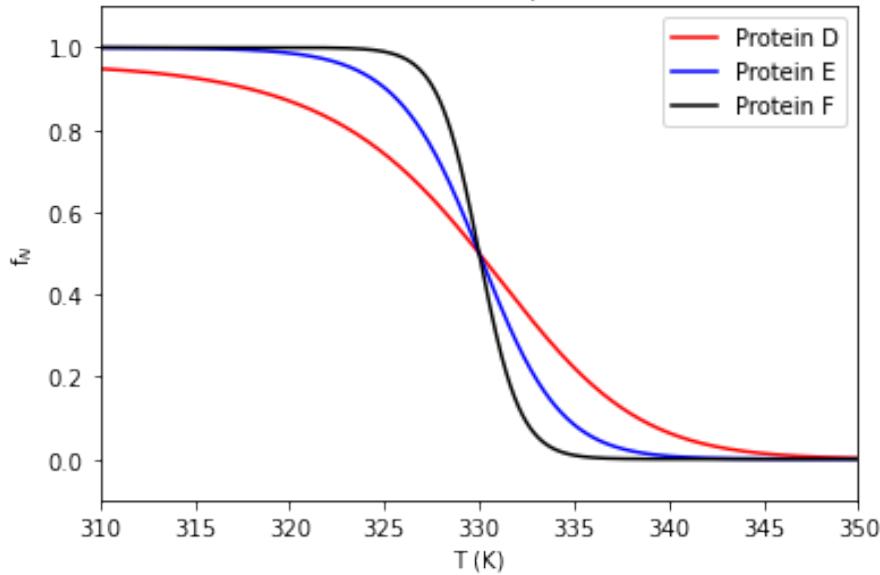
plt.plot(Ts, D, 'r', label="Protein D")
plt.plot(Ts, E, 'b', label="Protein E")
plt.plot(Ts, F, 'k', label="Protein F")
plt.axis([310,350,-0.1,1.1])
plt.ylabel("f$_-[N]$")
plt.xlabel("T (K)")
```

```

plt.title("Plot of Fraction Native as a Function of Temperature for Proteins of Varied  $\Delta H_{Tm}$ ")
plt.legend();

```

Plot of Fraction Native as a Function of Temperature for Proteins of Varied ΔH_{Tm}



0.0.4 Problem 5.5

Part A

```

[10]: lyz_data = pd.read_csv('./lyz_pH25.txt', sep='\t', header=None)
X = np.array(lyz_data[0])

X = np.array([i + 273.15 for i in X])
Y = np.array(lyz_data[1])

plt.plot(X[20:-10], Y[20:-10], 'o', color='lightcoral')
plt.ylabel("CD (mdeg)")
plt.xlabel("T (K)")
plt.title("Plot of CD vs T Curve for Protein Unfolding")

def Yn(T, a, b):
    Yn = a*T + b
    return Yn

def Yd(T, c, d):
    Yd = c*T + d
    return Yd

```

```

def lysozymefit(T, Tm, DH, a, b, c, d):
    YN = a*T + b
    YD = c*T + d
    R = 8.3145e-3 #KJ/mol K
    K = np.exp((DH * (T-Tm))/(R*T*Tm))
    #print(K)
    Yobs = YD + (((YN - YD)*K)/(1+K))
    return Yobs

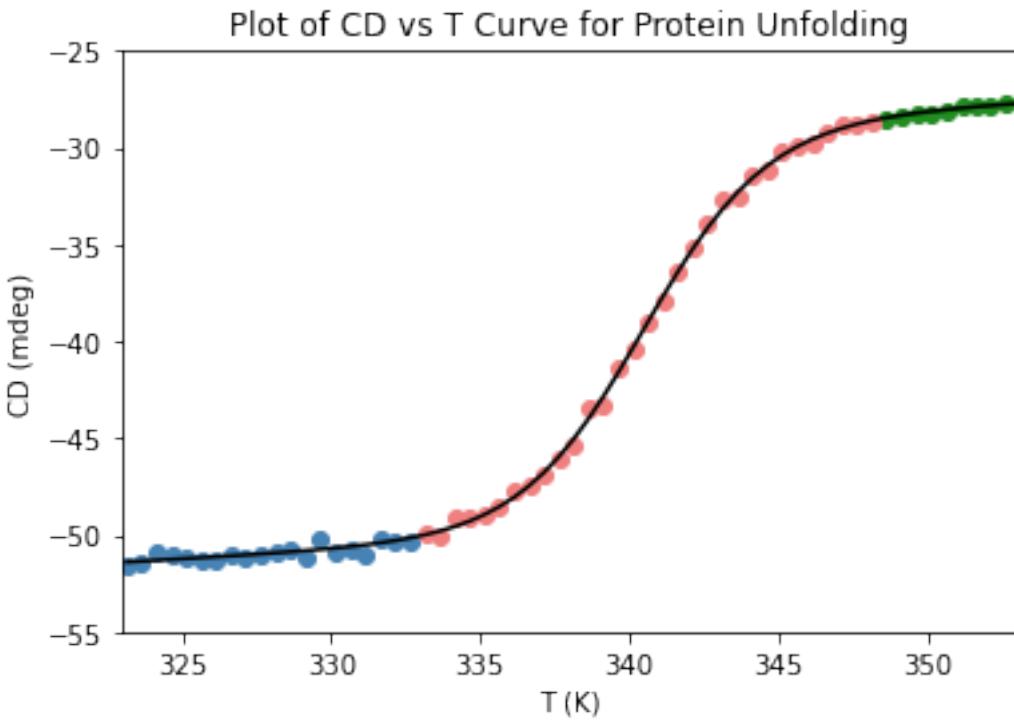
#N[:20] D: [-10:]
Nx = np.array(X[:20])
Ny = np.array(Y[:20])
Nguess = [1, -60]
npopt, npcov = curve_fit(Yn, Nx, Ny, Nguess)
#plt.plot(Nx, Yn(Nx, *npopt), 'steelblue')
plt.scatter(Nx, Ny, color='steelblue')

Dx = np.array(X[-10:])
Dy = np.array(Y[-10:])
Dguess = [2, -40]
dpopt, dpcov = curve_fit(Yd, Dx, Dy, Dguess)
plt.plot(Dx, Yd(Dx, *dpopt), 'g')
plt.scatter(Dx, Dy, color='forestgreen')
#print(npopt, dpopt)

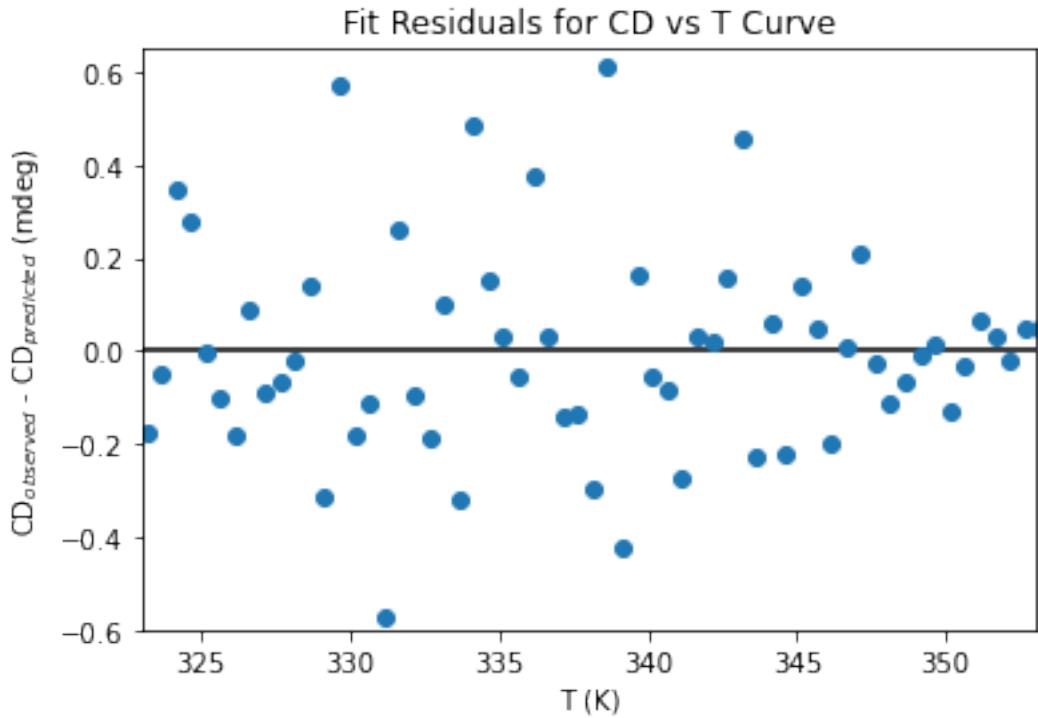
guesses = [342, -400, npopt[0], npopt[1], dpopt[0], dpopt[1]]

popt, pcov = curve_fit(lysozymefit, X, Y, guesses)
#popt[1] = -2179 #sets the DH to the ideal from Cp given in 5.5B. Is very
#clearly not correct for this data.
plt.plot(X, lysozymefit(X, *popt) , 'k');
plt.axis([323,353,-55, -25])

'''perr = np.sqrt(np.diag(pcov))
for i,j in enumerate(popt):
    print(f'{j} +/- {perr[i]}');
```



```
[11]: residuals = Y - lysozymefit(X, *popt)
plt.plot(X, residuals, 'o')
plt.hlines(0,300,400, 'k')
plt.axis([323,353,-0.6, 0.65])
plt.title("Fit Residuals for CD vs T Curve")
plt.xlabel("T (K)")
plt.ylabel("CD_{observed} - CD_{predicted} (mdeg);")
```



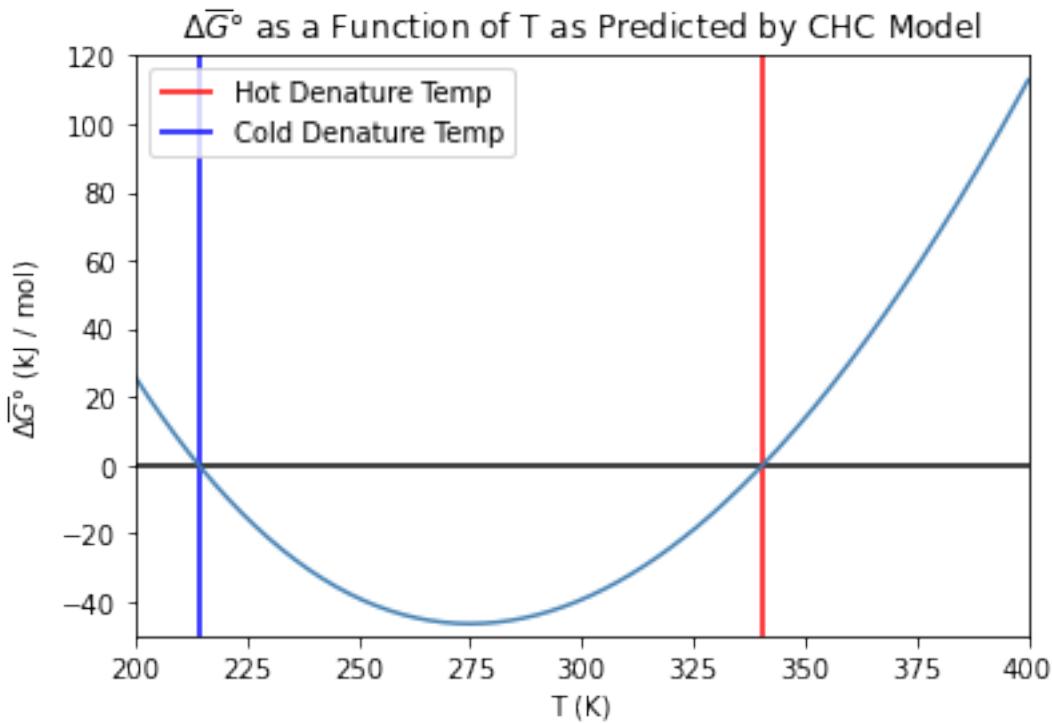
Part B

```
[12]: DH_pred = popt[1]
Tm_pred = popt[0]
DCp = -6.4 #kJ/mol K

def DGstdbar(T, Tm, DH, Cp):
    return DH + (Cp*(T-Tm)) - (T*D�/Tm) - T*Cp*np.log(T/Tm)

Ts = np.arange(200, 401, 1)
Gs = DGstdbar(Ts, Tm_pred, DH_pred, DCp)

plt.plot(Ts, Gs, 'steelblue')
plt.title("$\Delta\overline{G}^\circ$ as a Function of T as Predicted by  
→CHC Model")
plt.xlabel("T (K)")
plt.ylabel("$\Delta\overline{G}^\circ$ (kJ / mol)")
plt.axis([200, 400, -50, 120]);
plt.hlines(0,100,500,'k');
plt.vlines(Tm_pred, -50, 130, color='r', label="Hot Denature Temp")
plt.vlines(214.326, -50, 130, color='b', label="Cold Denature Temp")
plt.legend();
```



Part C

```
[17]: DG_350 = DGstdbar(350, Tm_pred, DH_pred, DCp)
DG_310 = DGstdbar(310, Tm_pred, DH_pred, DCp)

print(DG_350, 'kJ/mol', DG_310, 'kJ/mol')
```

13.78510531219272 kJ/mol -32.72397268695846 kJ/mol

Part D

```
[14]: DGstdbar(214.32587, Tm_pred, DH_pred, DCp)
#should be zero and it is
```

[14]: 7.80285347445897e-06