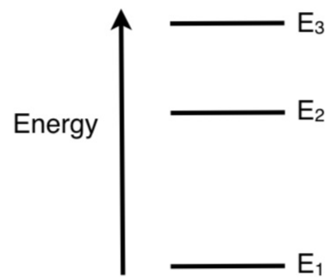
8. Thermodynamics/Statistical Physics

A solution in equilibrium at absolute temperature T contains a large number of the same type of protein molecules. The internal states of a protein molecule are arranged as follows:



Using the fundamental definition of entropy, $S = -R \sum_j P_j \, ln \, P_j$, determine an expression for the Helmholtz free energy of the internal states of one mole of these protein molecules. Your expression should be expressed in terms of E_1, E_2, E_3 and physical constants. Collect terms to simplify your answer.

$$R = N_A k_B$$

$$\Rightarrow \frac{S}{N_A} = -k_B \sum_j P_j \ln P_j$$

Now, $$P_j = \frac{1}{Z} e^{-\beta E_i}$$

$$\beta = \frac{1}{k_B T}$$

$$Z = \sum_i e^{-E_i \beta}$$

Note: NOT taking degeneracy into account.

$$\frac{S}{N_A} = -k_B \sum_j p_j \ln\left(\frac{1}{Z} e^{-\beta_j E_j}\right)$$

$$= -k_B \sum_j p_j \left[-\beta_j E_j - \ln(Z)\right]$$

$$= k_B \left(\frac{\overbrace{\sum_j p_j E}^{U/N_A}}{k_B T} + \ln Z \underbrace{\sum_j p_j}_{=1} \right)$$

$$\frac{S}{N_A} = \frac{U}{N_A T} + k_B \ln Z$$

$$S T = U + N_A k_B T \ln Z$$

$$\Rightarrow \quad U - TS = -N_A k_B \ln Z$$

Now, $\quad F = U - TS$

Note: Mathematically, this is a Legendre trasformation of $U(S, V)$ to $F(T, V)$ since

$$\begin{aligned} dF &= dU - d(TS) \\ &= TdS - PdV - TdS - SdT \\ &= -SdT - PdV \end{aligned}$$

Therefore,

$$F = -N_A k_B T \ln Z$$

$$\Rightarrow \boxed{F = -RT \ln Z}$$

$$\boxed{F = -RT\ln\left(e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}\right)}$$