Statistical Molecular Thermodynamics

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Video 6.7

β and Boltzmann’s Constant
Circling Back to $\beta$

Given: \[ S = -k_B \sum_j p_j \ln p_j \]

we can differentiate to determine:

\[ dS = -k_B \left( \sum_j \ln p_j dp_j + \sum_j dp_j \right) \]

\[ = -k_B \sum_j \ln p_j dp_j \]

\[ dS = -k_B \sum_j \left( -\beta E_j - \ln Q \right) dp_j \]

\[ = k_B \beta \sum_j E_j dp_j + k_B \ln Q \sum_j dp_j \]

\[ = k_B \beta \sum_j E_j dp_j \]

\[ p_j = \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)} \]

sum of all probabilities is a constant (1)

again using: $p_j = \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$
Circling Back to $\beta$

\[ dS = k_B \beta \sum_j E_j dp_j \]

From Video 5.6:  
\[ dU = \sum_j p_j dE_j + \sum_j E_j dp_j = \sum_j p_j \left( \frac{\partial E_j}{\partial V} \right)_N dV + \sum_j E_j dp_j \]

Compare this to  
\[ dU = \delta w_{\text{rev}} + \delta q_{\text{rev}} \]

So,  
\[ dS = k_B \beta \delta q_{\text{rev}} \quad \text{But also,} \quad dS = \frac{\delta q_{\text{rev}}}{T} \]

\[ k_B \beta = \frac{1}{T} \quad \beta = \frac{1}{k_B T} \quad \text{Q.E.D.} \]

The connection between statistical and classical thermodynamics is established.