Statistical Molecular Thermodynamics

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Video 6.7

β and Boltzmann's Constant

Circling Back to β

Given: $$S = -k_B \sum_j p_j \ln p_j$$

we can differentiate to determine:

sum of all probabilities is a constant (1)

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

$$= -k_B \sum_j \ln p_j dp_j$$

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

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

$$= k_B \beta \sum_j E_j dp_j + k_B \ln Q \sum_j dp_j$$

$$= k_B \beta \sum_j E_j dp_j$$

Circling Back to β

$$dS = k_B \beta \sum_j E_j dp_j$$

the same

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

$E_j = E_j(N,V)$

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

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

$\Rightarrow$ $k_B \beta = \frac{1}{T}$ $\Rightarrow$ $\beta = \frac{1}{k_B T}$ Q.E.D.

The connection between statistical and classical thermodynamics is established