Statistical Molecular Thermodynamics

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Video 6.6

Entropy and the Partition Function
Entropy: Probability Form

Recall from Video 6.4: \( S_{\text{ensemble}} = k_B \left( A \ln A - \sum_j a_j \ln a_j \right) \)

where \( A \) is the total number of systems in the ensemble, and \( a_j \) is the population of each system \( j \).

Then the average system entropy is \( S_{\text{ensemble}} / A \) and the probability \( p_j \) of choosing a system in state \( j \) is \( a_j / A \); or, \( a_j = p_j A \)

Then: \( S_{\text{ensemble}} = k_B \left( A \ln A - \sum_j p_j A \ln p_j A \right) \)

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

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

\( S_{\text{system}} = -k_B \sum_j p_j \ln p_j \)
Entropy: Probability Form

\[ S_{\text{system}} = -k_B \sum_j p_j \ln p_j \]

Note that L'Hôpital's rule establishes that \( \lim_{x \to 0} x \ln x = 0 \)

If all probabilities are 0 except one: \( S = 0 \)

If all probabilities are equal: \( S \) is maximized

Recall, in the \( NV\beta \) ensemble: \( p_j = \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)} \)

\[ S = -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \ln \left( \frac{e^{-\beta E_j}}{Q} \right) = -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \left( -\beta E_j - \ln Q \right) \]
Entropy and the Partition Function

\[ S = -k_B \sum_j e^{-\beta E_j} \left( -\beta E_j - \ln Q \right) \]

Some manipulation:

\[ S = \frac{1}{T} \sum_j p_j E_j + \frac{k_B \ln Q}{Q} \sum_j e^{-\beta E_j} \]

\[ = \frac{U}{T} + k_B \ln Q \]

\[ = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \]

\( S \) can be computed directly from partition function!
**Entropy of a Monatomic Ideal Gas**

\[ Q = \frac{1}{N!} \left( \frac{2\pi mk_B T}{h^2} \right)^{3N/2} V^N g_{e_1}^N \]

\[ \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = \frac{3N}{2} \left( \frac{1}{T} \right) \]

\[ \ln Q = N \ln \left[ \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} V g_{e_1} \right] - \ln N! \]

\[ = N \ln \left[ \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} V g_{e_1} \right] - N \ln N + N \]

\[ = N \ln \left[ \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{V}{N} g_{e_1} \right] + N \]

\[ S = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \]
Entropy of a Monatomic Ideal Gas

\[ Q = \frac{1}{N!} \left( \frac{2\pi mk_B T}{h^2} \right)^{3N/2} V^N g_{e1}^N \]

\[ \ln Q = N \ln \left[ \left( \frac{2\pi kmk_B T}{h^2} \right)^{3/2} V \right] + N \]

\[ \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = \frac{3N}{2} \left( \frac{1}{T} \right) \]

\[ S = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \]

If \( N = N_A \) (molar quantity):

\[ \bar{S} = \frac{5}{2} R + R \ln \left[ \left( \frac{2\pi kmk_B T}{h^2} \right)^{3/2} \frac{V g_{e1}}{N_A} \right] \]

Entropy increases with 1) increasing mass \( m \), 2) increasing temperature \( T \), 3) increasing standard-state volume \( V \), and 4) increasing electronic ground-state degeneracy \( g_{e1} \)