Statistical Molecular Thermodynamics

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Video 6.6

Entropy and the Partition Function

Entropy: Probability Form

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

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_{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: $S_{\text{ensemble}} = k_{\text{B}}\left(A \ln A - \sum_j p_j A \ln p_j A \right)$

$$= k_{\text{B}} A \ln A - k_{\text{B}} A \sum_j p_j \ln p_j - k_{\text{B}} A \ln A \sum_j p_j$$

sum of all probabilities is 1

$$= -k_{\text{B}} A \sum_j p_j \ln p_j \quad \Rightarrow \quad \boxed{S_{\text{system}} = -k_{\text{B}} \sum_j p_j \ln p_j}$$

Entropy: Probability Form

$$S_{\text{system}} = -k_{\text{B}} \sum_j p_j \ln p_j$$

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

$$\Rightarrow \quad S = -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \ln\left(\frac{e^{-\beta E_j}}{Q}\right) = -k_B \sum_j \frac{e^{-\beta E_j}}{Q}\left(-\beta E_j - \ln Q\right)$$

Entropy and the Partition Function

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

Some manipulation:

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

$$= \frac{U}{T} + k_B \ln Q$$

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

sum is Q

probability weighted energy
is internal energy U

S can be computed directly from partition function!

Entropy of a Monatomic Ideal Gas

$$Q = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} V^N g_{e1}^N$$

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

$$\ln Q = N \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V g_{e1}\right] - \ln N!$$

$$= N \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V g_{e1}\right] - N \ln N + N$$

$$= N \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{V}{N} g_{e1}\right] + N$$

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

Entropy of a Monatomic Ideal Gas

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

If $N = N_A$ (molar quantity):

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

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}