Statistical Molecular Thermodynamics

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Video 6.4

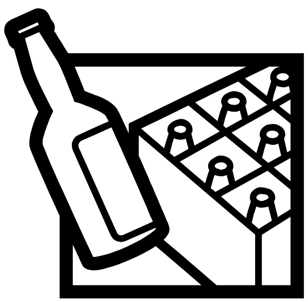
Statistical Entropy

Recalling Boltzmann

$$\boxed{S = k_{\mathrm{B}} \ln W}$$

Entropy is a state function related to the disorder of a system. Disorder can be expressed in a number of ways… here is a good one:

Remember the water cooler?



Last time we had each bottle (system) in the collection of bottles (ensemble) having the same $\boldsymbol{N}$, $\boldsymbol{V}$, and $\boldsymbol{T}$. (This is called a *canonical ensemble*.)

This time let's create a collection of bottles (ensemble) where each bottle (system) has the same $\boldsymbol{N}$, $\boldsymbol{V}$, and $\boldsymbol{E}$. (This is called a *<u>micro</u>canonical ensemble*.)

Even though every system has the same energy, each system can be in a different quantum state thanks to degeneracy.

$\Omega(E)$ is the degeneracy associated with energy E

this number is typically huge!

Some Multinomial Statistics

Let W be the number of ways of having a_1 systems in state 1, a_2 in state 2, etc. (the systems are distinguishable)

number of ways to order A things

$$W(a_1, a_2, a_3, \ldots) = \frac{A!}{a_1! a_2! a_3! \ldots} = \frac{A!}{\prod_j a_j!}$$

reduction based on how many ways each subgroup can be ordered

An example: $A = \sum_i a_i = 4$

$a_1 = 2, a_2 = 2, a_3 = 0, a_4 = 0, W = 6$

1	2	1	2	1	1
1	2	2	1	2	2
2	1	2	2	2	1
2	1	1	1	1	2

Other possibilities:

$a_1 = 1, a_2 = 2, a_3 = 1, a_4 = 0, W = 12$

$a_1 = 1, a_2 = 1, a_3 = 1, a_4 = 1, W_{max} = 24$

$a_1 = 4, a_2 = 0, a_3 = 0, a_4 = 0, W_{min} = 1$

$a_1 = 3, a_2 = 0, a_3 = 1, a_4 = 0, W = 4$

Additivity of the Entropy

$$S = k_{\mathrm{B}} \ln W$$

For a perfectly ordered arrangement: $W = 1,\ S = 0$

For the most disordered arrangement: W and S are maximized

$\ln W$ form is consistent with the additivity of the entropy and the product character of ensemble arrangements

$$S_{total} = S_A + S_B \qquad W_{AB} = W_A W_B$$

$$S_{total} = k_{\mathrm{B}} \ln W_{AB} = k_{\mathrm{B}} \ln W_A W_B = k_{\mathrm{B}} \ln W_A + k_{\mathrm{B}} \ln W_B$$

The Degeneracy Form

$$S = k_\mathrm{B} \ln \frac{A!}{\prod_j a_j!} = k_\mathrm{B}\left(\ln A! - \sum_j \ln a_j!\right)$$

Stirling's approximation: $\ln N! = N \ln N - N$

$$S = k_\mathrm{B}\left(\ln A! - \sum_j \ln a_j!\right)$$

$$= k_\mathrm{B}\left(A \ln A - A - \sum_j a_j \ln a_j + \sum_j a_j\right)$$

$$= k_\mathrm{B}\left(A \ln A - \sum_j a_j \ln a_j\right)$$

Let the number of degenerate states j available be Ω

Let the population of each degenerate state be $a_j = n$ (W is maximized when all states have equal populations)

Then the total number of systems is $A = n\Omega$

The Degeneracy Form

$$S = k_\mathrm{B}\left[n\Omega\ln(n\Omega) - \sum_{j=1}^{\Omega} n\ln n\right] = k_\mathrm{B}\left[n\Omega\ln(n\Omega) - n\Omega\ln n\right]$$

$$= n\Omega k_\mathrm{B}\ln(\Omega) = k_\mathrm{B}\ln\left(\Omega_\mathrm{system}\right)^{A} = k_\mathrm{B}\ln\left(\Omega_\mathrm{ensemble}\right)$$

$$S = k_\mathrm{B}\ln\Omega$$

Consider a specific example, the isothermal expansion of an ideal gas

$$\Omega = f(N)g(E)V^{N}$$

N ideal gas molecules

Isothermal Expansion Example

$$\Omega = f(N)g(E)V^N$$

$$\begin{aligned}
\Delta\overline{S}_{1\rightarrow 2} &= k_{\mathrm{B}}\ln\Omega_2 - k_{\mathrm{B}}\ln\Omega_1 \\
&= k_{\mathrm{B}}\ln\frac{f(N)g(E)V_2^{N_A}}{f(N)g(E)V_1^{N_A}} \\
&= k_{\mathrm{B}}\ln\left(\frac{V_2}{V_1}\right)^{N_A} \\
&= R\ln\frac{V_2}{V_1}
\end{aligned}$$

no change in number, and isothermal, so no change in energy

as derived previously using first and second law analyses