Biophysical Chemistry for Life Scientists

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Lecture 4
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Entropy and Free Energy. Second and Third Laws of Thermodynamics.

- **What is Entropy?**

Entropy is a state function, or property of a system, that provides a measure of its disorder or randomness.

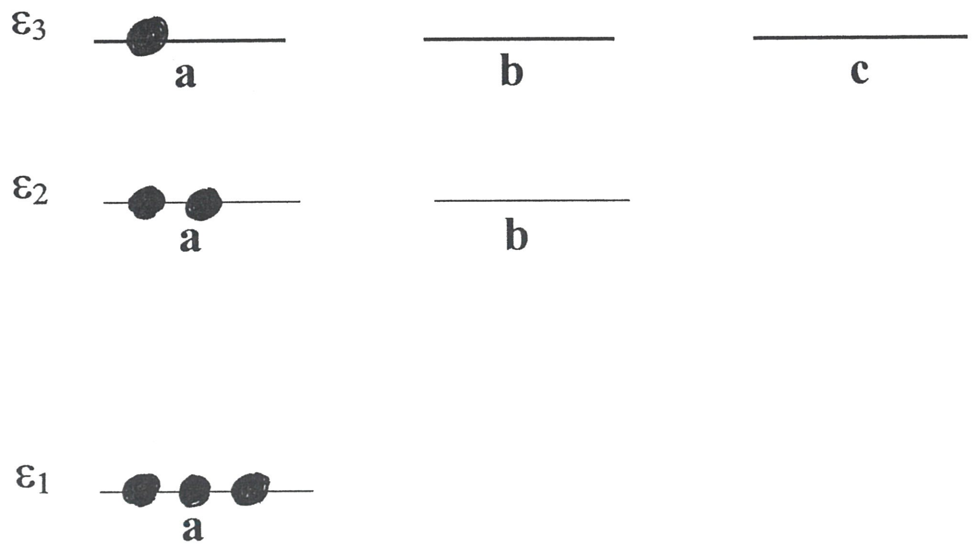
It is an extensive property. It is a function of T and V (or P), and chemical composition.

- **<u>What do we mean by disorder or randomness?</u>**

Illustrate by way of an example.

Return to the system of non-interacting or weakly interacting particles discussed earlier.

For simplicity, we pick a system of six non-interacting particles. Suppose, the particles occupy energy states with energies equal to ε_1, ε_2, and ε_3 as follows:



$$\text{Then,} \quad E_{system} = 3\,\varepsilon_{1a} + 2\,\varepsilon_{2a} + \varepsilon_{3a}$$

$$= 3\,\varepsilon_1 + 2\,\varepsilon_2 + \varepsilon_3$$

$$N_{system} = n_{1a} + n_{2a} + n_{3a}$$

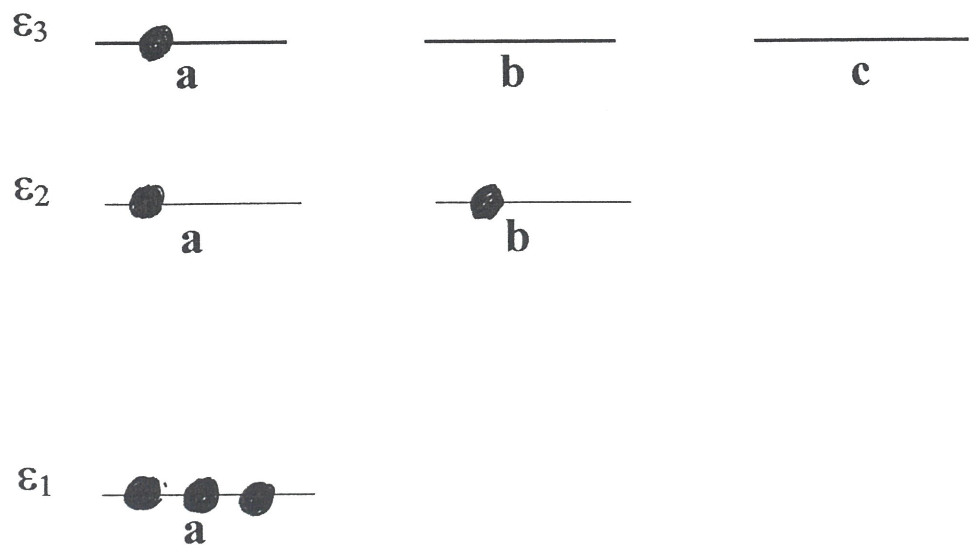
$$= 3 + 2 + 1 = 6$$

and the wavefunction for the system is

$$\Psi_1(1,2,3,4,5,6)$$

$$= \phi_{1a}(1)\, \phi_{1a}(2)\, \phi_{1a}(3)\, \phi_{2a}(4)\, \phi_{2a}(5)\, \phi_{3a}(6)$$

However, if there are degeneracies associated with the molecular energy levels, namely, there are energy states of equal energy associated with the energy levels, which is typically the case, then there are other particle distributions with the same E_{system}. For example,



Here, for this particle distribution,

$$E_{system} = 3\,\varepsilon_{1a} + \varepsilon_{2a} + \varepsilon_{2b} + \varepsilon_{3a}$$

$$= 3\,\varepsilon_1 + 2\,\varepsilon_2 + \varepsilon_3$$

$$N_{system} = n_{1a} + n_{2a} + n_{2b} + n_{3a}$$

$$= 3 + 1 + 1 + 1 = 6$$

as before, but the wavefunction for the system is different:

$$\Psi_2(1,2,3,4,5,6)$$

$$= \phi_{1a}(1)\,\phi_{1a}(2)\,\phi_{1a}(3)\,\phi_{2a}(4)\,\phi_{2b}(5)\,\phi_{3a}(6)$$

$$\uparrow \quad \uparrow$$

Because of equal a priori probability for the particles to occupy molecular energy states of the same energy, this particle distribution is just as likely as the first one. In other words, it is equally likely for the system to be represented by Ψ_1 or Ψ_2.

Other particle distributions are obtained by redistributing the particles among the degenerate molecular energy states associated with the energy levels, and there would be a distinct wavefunction for each.

We could generalize this to a system of N particles (N approaching N_A) with electronic, vibrational, rotational, translational degrees of freedom, where the molecular energy levels are highly packed and degenerate, as we discussed earlier. Thus, for a given E_{system}, the system could be represented by many, many system wavefunctions (Ψ_{system}), corresponding to the different ways of distributing the particles among the molecular quantum states.

To illustrate this outcome, I appeal to a system of N non-interacting particles. However, this result is completely general, and applies to any system involving large numbers of molecules. Thus, for macroscopic systems, in practice, the system has a high density of system states, namely, there are many, many Ψ_{system} 's with the same E_{system}.

E_{system}

- **<u>Definition of Statistical Entropy</u>**

$$\text{Entropy} = S = k_B \ln \Omega_{system}$$

where Ω_{system} is the total number of system wavefunctions associated with the system for a given E_{system}.