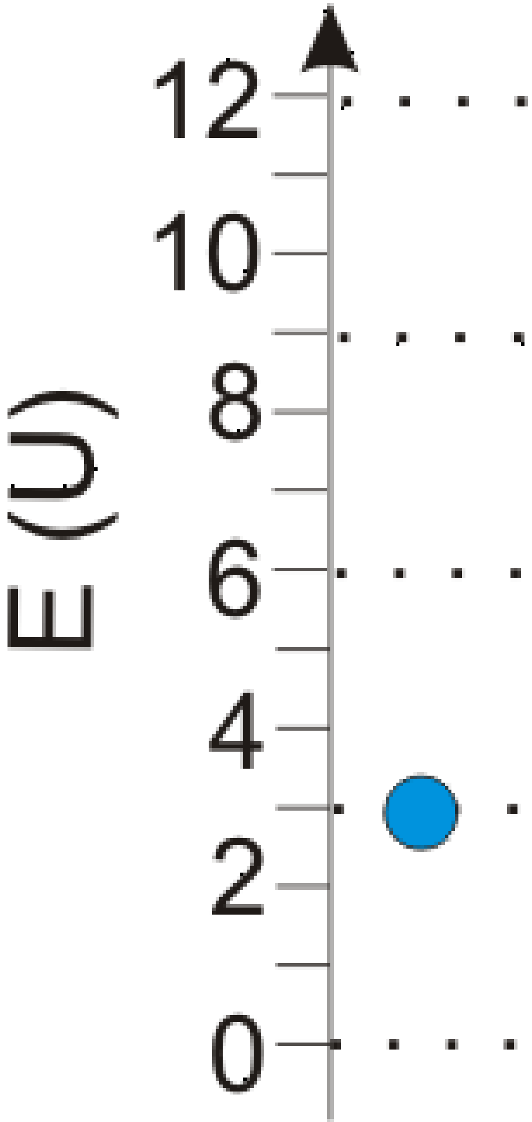
A statistical view of entropy

We can make entropy quantitative by understanding the microscopic factors that govern the distribution of energy. Entropy is determined by how many energy states are available. Using statistics we can count how many states are accessible. For molecules we may count translational, rotational and vibrational states. For polymers and macro-molecules in solution we count conformational states. In this section we will consider the quantitative ways to count how many conformations are accessible, both to collections of molecules and to macromolecules. These methods are useful for understanding entropy and in a number of Specific applications. You may also learn how to win at Poker if you are clever.

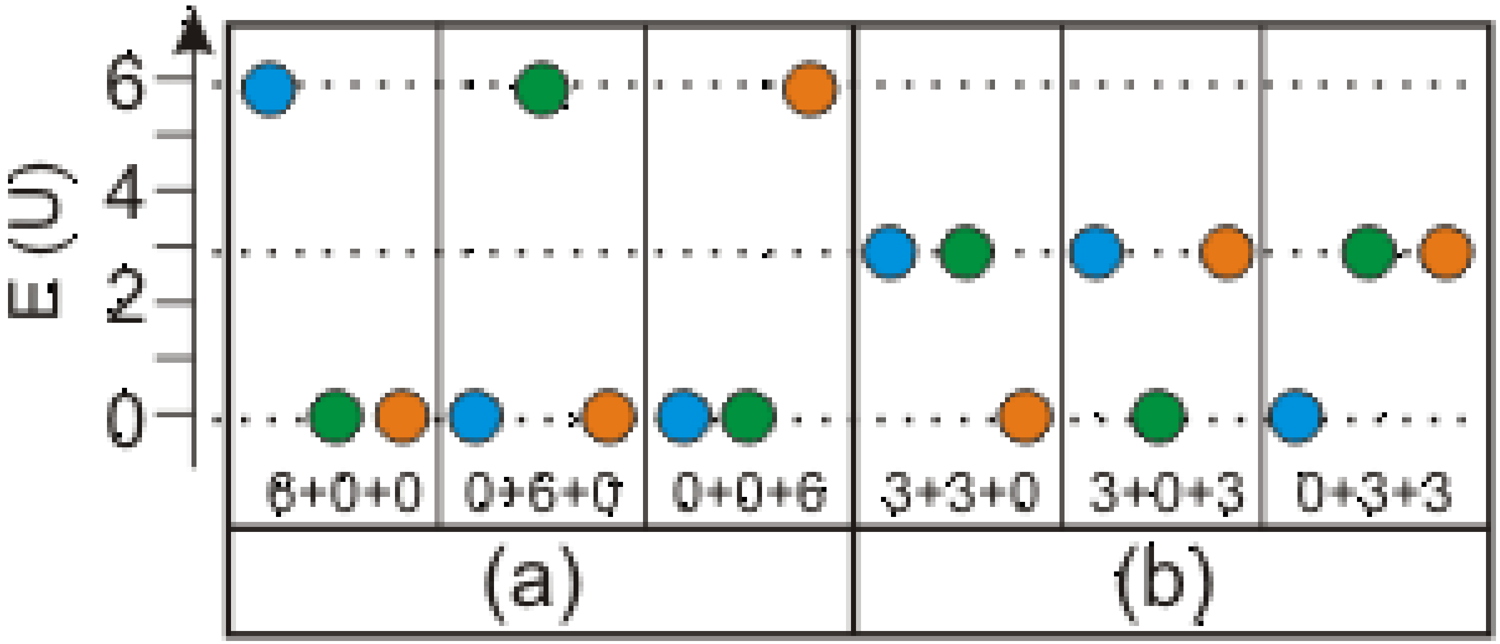
Entropy is proportional to the number of ways that energy can be distributed



Energy of molecule (E_m) is quantized

(arbitrary units U)

Distribute 6 units of E among 3 molecules



config a
W = 3

config b
W = 3

<u>6 total ways to distribute 6 units of E</u>

Counting ways to distribute energy

In the example we have 3 particles in each configuration. Such that

$$E_{total} = \sum_{\substack{allowed \\ energies}} n_i E_i$$

For each configuration we have a different set of n_i. If we have N total particles (here N=3), then the total number of ways to distribute the particles among the allowed energy levels is determine by the factorial.

Statistical distribution among energies

In the example we have 3 particles in each configuration. Such that

$$W = \frac{N!}{\prod_i n_i!}$$

where the exclamation sign is the factorial. For example, 4! = 4 x 3 x 2 x 1 = 24. In the above examples we can calculate the number of ways to distribute the energy.

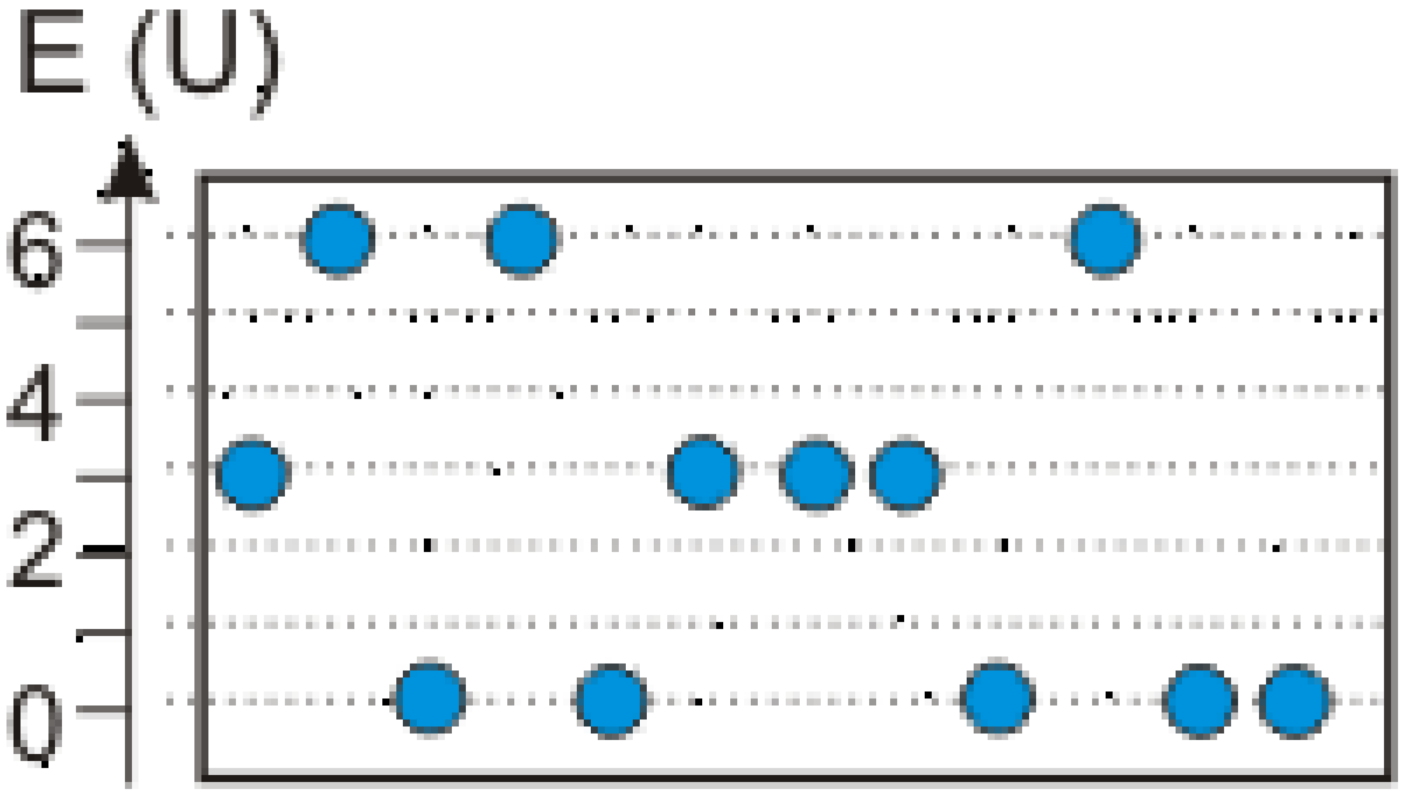
Statistical distribution among energies

In this case once we have determined the occupation numbers we can just plug those into the factorial. For configuration a
We have $n_0 = 2$, $n_1 = 0$ and $n_2 = 1$.

$$W = \frac{3!}{2!\,0!\,1!} = 3$$

Although the actual occupied levels are not the number of occupied levels is statistically the same, $n_0 = 1$, $n_1 = 2$ and $n_2 = 0$.

$$W = \frac{3!}{1!\,2!\,0!} = 3$$



Total E:
30 U

$$W = \frac{12!}{(5!)\,(0!)\,(0!)\,(4!)\,(0!)\,(0!)\,(3!)}$$

$$= 27720$$

Statistics of Yahtzee die casts

Total die casts

$$W = M^N = 6^5 = 7776$$

Probability of a large straight

$$W = \frac{N!}{n_1!\, n_2!\, n_3!\, n_4!\, n_5!\, n_6!}$$

$$W_{large\ straight} = \frac{5!}{1!\, 1!\, 1!\, 1!\, 1!\, 0!} = 120$$

Probability of a large straight

There are 2 possible large straight combinations. Thus,

$$P_{large\ straight} = \frac{120\ x\ 2}{7776} = 0.03\ or\ 3\%$$

Probability of a full house

$$W = \frac{N!}{n_1!\, n_2!\, n_3!\, n_4!\, n_5!\, n_6!}$$

$$W_{full\ house} = \frac{5!}{0!\, 0!\, 2!\, 3!\, 0!\, 0!} = 10$$

Probability of a full house

There are 30 possible full house combinations. Thus,

$$P_{full\ house} = \frac{30\ x\ 10}{7776} = 0.038\ or\ 3.8\%$$

Probability of a Yahtzee

$$W = \frac{N!}{n_1!\,n_2!\,n_3!\,n_4!\,n_5!\,n_6!}$$

$$W_{Yahtzee} = \frac{5!}{0!\,0!\,0!\,0!\,0!\,5!} = 1$$

Probability of a Yahtzee

There are 6 possible Yahtzee combinations.
Thus,

$$P_{Yahtzee} = \frac{6\ x\ 1}{7776} = 0.0007\ or\ 0.07\%$$

Chemical applications statistics

The point of the exercise with Yahtzee is to help you remember the meaning of total number particles and energy states. In the Yahtzee analogy the number of dice is the number of particles and the number of die casts (for each die) is the number of energy states. The statistics help us to combine those values for an individual particle and calculate the value for a system. This is useful on a very large scale for statistical thermodynamics. Hopefully, it helps you to realize that entropy is defined by how many ways we can distribute particles among states of the same energy.

Combinatoric and factorial

The other quantity that we see in the Yahztee analogy is the total number of states accessible. That is given by:

$$W = M^N$$

We call this the combinatoric. We can use this for understanding the conformations of macromolecules. In cases where not all of the states are equally accessible we can use the factorial.

$$W = \frac{N!}{n_1!\,n_2!\,n_3!\,n_4!\,n_5!\,n_6!}$$

Here it is shown for six possible states, but there could be any number in theory.