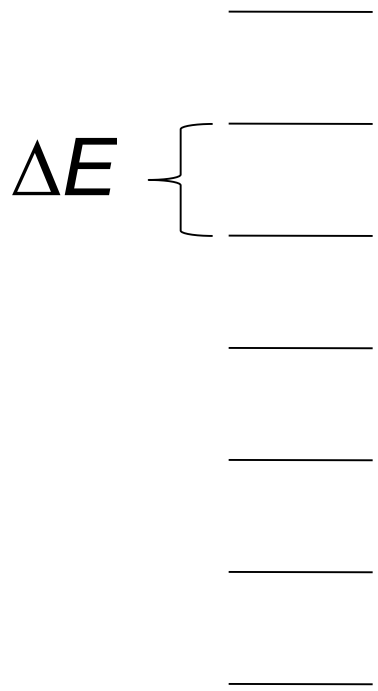
Extension to an energy ladder

If we have a system with an infinite number of equally spaced energy levels we can calculate the probability and energy using statistical methods as well.

$$P_n = \frac{e^{-\frac{nE}{k_BT}}}{1 + e^{-\frac{E}{k_BT}} + +e^{-\frac{2E}{k_BT}} + e^{-\frac{3E}{k_BT}} + \cdots.} = \frac{e^{-nE/k_BT}}{Q}$$



We have defined Q, which is known as the partition function. It is apparently an infinite sum. Fortunately, it can be simplified.

Partition function for an energy ladder

The denominator of the probability expression contains Q, the partition function. Q gives the average number of levels that are accessible at a given temperature.

$$Q = 1 + e^{-\frac{E}{k_B T}} + +e^{-\frac{2E}{k_B T}} + e^{-\frac{3E}{k_B T}} + \cdots$$

Using the substitution

$$x = e^{-\frac{E}{k_B T}}$$

We can write the partition function as

$$Q = 1 + x + x^2 + x^3 + x^{4.} + \cdots = \sum_{n=0}^{\infty} x^n$$

Writing the partition function in closed form

Since Q is geometric series we can write it in closed form.
First, we see that subtracting 1 from the series yields:

$$Q - 1 = x + x^2 + x^3 + x^{4.} + \cdots$$

Multiplying the series by x yields the same result:

$$xQ = x + x^2 + x^3 + x^{4.} + \cdots$$

We can equate the left hand side of each equation:

$$xQ = Q - 1$$

We solve for Q to obtain:

$$Q = \frac{1}{1 - x} = \frac{1}{1 - e^{-E/k_B T}}$$

Average energy of an energy ladder

To obtain the energy we can consider the general formula and make the substitution β = 1/kT.

$$< E \succ = \sum_{n=0}^{\infty} P_n E_n = \frac{Ee^{-\beta E} + 2\mathrm{E}e^{-2\beta E} + 3\mathrm{E}e^{-3\beta E} + \cdots.}{1 + e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + \cdots.}$$

This ratio can be simplified by noting that there is a relationship between the numerator and the denominator. We have already seen that the denominator is Q, the partition function. Therefore, the numerator is:

$$-\frac{\partial Q}{\partial \beta} = Ee^{-\beta E} + 2\mathrm{E}e^{-2\beta E} + 3\mathrm{E}e^{-3\beta E} + \cdots.$$

Average energy of an energy ladder

Because of this relationship, there is a compact way to write the average energy in closed form:

$$< E > = -\frac{\frac{\partial Q}{\partial \beta}}{Q} = -\frac{\partial\, lnQ}{\partial \beta}$$

We can use this result to obtain the average energy for a evenly spaced energy ladder:

$$< E > = \frac{e^{-E/k_B T} E}{1 - e^{-E/k_B T}}$$

Usually the average energy is written in the form:

$$< E > = \frac{E}{e^{E/k_B T} - 1}$$

High temperature limit of the energy

As the temperature approaches infinity all of the levels become equally populated. The average energy can be calculated assuming $\beta = 1/kT << 1$.

$$< E >= \frac{E}{e^{E/k_BT} - 1} = \frac{E}{1 + E/k_B T + \cdots - 1} = k_BT$$

Thus, kT is a classical energy for an averaged system at high temperature. In units of joules/mole

$$< E > = RT$$

The energy of a gas is related to its PV_m product (V_m is the molar volume) thus,

$$PV_m = RT$$