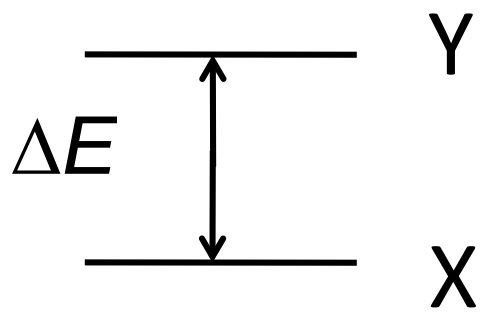
Microscopic probability

When we look at the world in terms of energy levels we can see that the probability of being in a given level depends on temperature. We define the probability of being in level j as

$$P_j = \frac{number\ \ of\ molecules\ in\ state\ \ j}{total\ number\ \ of\ molecules}$$

The two level system is given by the following levels



Microscopic probability in a two level system

We can calculate the probability of levels X and Y

$$P_X = \frac{N_X}{N_X + N_Y} = \frac{1}{1 + N_Y/N_X} = \frac{1}{1 + e^{-\Delta E/kT}}$$

$$P_Y = \frac{N_Y}{N_X + N_Y} = \frac{N_Y/N_X}{1 + N_Y/N_X} = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$$

Of course, $P_X + P_Y = 1$

Average energy for a two level system

We defined the relative energy of the two states as

$$\Delta E = E_Y - E_X.$$

We can (arbitrarily) set the energy of state X to zero,

$$E_X = 0.$$

Then the energy of state Y is $E_Y = \Delta E$.

The average energy of the system is:

$$< E > = \sum_{i=1}^{\infty} P_j E_j = P_X E_X + P_Y E_Y$$

$$= \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} E_Y = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} \Delta E$$