Thermodynamics of materials

14. Partition Function

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The Partition Function

- The ratio of probability is

$$\frac{\mathsf{Prob}(2)}{\mathsf{Prob}(1)} = e^{\frac{-\Delta E}{k_\mathrm{B} T}} = \frac{e^{\frac{-E_2}{k_\mathrm{B} T}}}{e^{\frac{-E_1}{k_\mathrm{B} T}}}$$

- It can be rearranged by

$$\frac{\mathsf{Prob}(2)}{e^{\frac{-E_2}{k_\mathrm{B} T}}} = \frac{\mathsf{Prob}(1)}{e^{\frac{-E_1}{k_\mathrm{B} T}}} = \frac{1}{Z}$$

with introducing parameter Z.

- It means that

$$\mathsf{Prob}(1) = \frac{1}{Z} e^{\frac{-E_1}{k_\mathrm{B} T}}$$

in general,

$$P(s) = \frac{1}{Z} e^{\frac{-E_s}{k_\mathrm{B} T}} = \frac{1}{Z} e^{-\beta E_s} \qquad \beta = \frac{1}{k_\mathrm{B} T}$$

The Partition Function

- Since the summation of the probability is 1,

$$1 = \sum_{s=1}^{\infty} P(s) = \frac{1}{Z} \sum_{s=1}^{\infty} e^{\frac{-E_s}{k_\mathsf{B} T}}$$

therefore, we can derive the expression for Z, partition function by

$$Z = \sum_{s=1}^{\infty} e^{\frac{-E_s}{k_\mathsf{B} T}}$$

- For example, a ground state hydrogen atom has an energy of $E_0 = -13.6\,\text{eV}$, ground state energy, and all other excited states has the amount of $E_0 + \Delta E_s$, the possibility of the excited state s is

$$P(s) = \frac{1}{Z} e^{\frac{-(E_0 + \Delta E_s)}{k_\mathsf{B} T}} = \frac{1}{Z} e^{\frac{-(E_0)}{k_\mathsf{B} T}} e^{\frac{-(\Delta E_s)}{k_\mathsf{B} T}}$$

where

$$Z = \sum e^{\frac{-(E_0)}{k_\mathsf{B} T}} e^{\frac{-(\Delta E_s)}{k_\mathsf{B} T}} = e^{\frac{-(E_0)}{k_\mathsf{B} T}} \sum e^{\frac{-(\Delta E_s)}{k_\mathsf{B} T}}$$

therefore,

$$P(s) = \frac{e^{\frac{-(\Delta E_s)}{k_\mathsf{B} T}}}{\sum e^{\frac{-(\Delta E_s)}{k_\mathsf{B} T}}}$$

The constant offset of the ground state factors out.

The Partition Function

- At $T = 5772\,\mathrm{K}$, let $E_1 = -13.6\,\mathrm{eV}$, $E_2 = -3.4\,\mathrm{eV}$, $E_3 = -1.5\,\mathrm{eV}$ and $E_4 = -0.85\,\mathrm{eV}$. Then the partition function is

$$Z = e^{\frac{0}{0.497}} + e^{\frac{-10.2}{0.497}} + e^{\frac{-12.1}{0.497}} + e^{\frac{-12.75}{0.497}} = 1.00000000126$$

State	Probability
$n = 1$	0.999999999
$n = 2$	1.22×10^{-7}
$n = 3$	2.67×10^{-11}
$n = 4$	7.22×10^{-12}

Table: Energy state and corresponding probability