Thermodynamics of materials 13. Boltzmann Factor

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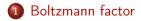
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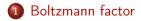
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Thermodynamics

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- With N inert gas atoms, which can have electrons in different energy state. Some will be in the ground state n = 1, and some could be in excited states with n > 1.
- If the gas is hotter, then more will be in exited states. How can we calculate the likelihood of an electrons in an excited state? We can calculate using Boltzmann factor.

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Boltzmann factor

• To evaluate likelihood that the electron is in an excited state (n = 2) compared to the ground state, n = 1, we can evaluate the likelihood using number of probable microstates

$$\frac{\mathsf{Prob}(2)}{\mathsf{Prob}(1)} = \frac{\Omega_2}{\Omega_1}$$

• For the state 1, the entropy with Ω_1 microstates, Boltzmann proposed that the entropy at state 1 is

$$S_1 = k_{\mathsf{B}} \ln \Omega_1$$

therefore,

$$\frac{\mathsf{Prob}(2)}{\mathsf{Prob}(1)} = \frac{\Omega_2}{\Omega_1} = \frac{e^{S_2/k_{\mathsf{B}}}}{e^{S_1/k_{\mathsf{B}}}} = e^{\Delta S/k_{\mathsf{B}}}$$

where

$$\Delta S = S_1 - S_2$$

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Boltzmann factor

• The thermodynamic identity to find the change in entropy:

$$\Delta S = \frac{\Delta U + p\Delta V - \mu\Delta N}{T}$$

• When the volume and number of atoms are fixed,

$$\Delta S = \frac{\Delta U}{T}$$

when system evolves from state 1 to 2,

$$\Delta S_{1\to 2} = \frac{U_2 - U_1}{T} = -\frac{E_2 - E_1}{T}$$

Minus sign is because the energy of the reservoir U and the energy of the atom E are negative of each other, which yields the Boltzmann factor.

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



• For a hydrogen atom, the ground state is known as $E_1 = -13.6 \text{ eV}$ and the energy of the first excited state is $E_2 = -3.4 \text{ eV}$. At T = 298 K, the ratio between liklihood of two states is

$$e^{\frac{-\Delta E}{k_{\mathsf{B}}T}} = e^{\frac{-10.2}{0.026}} = 4.2 \times 10^{-171}$$

• How about at $T = 5772 \,\mathrm{K}$, at temperature of the surface of the sun,

$$e^{\frac{-10.2}{0.497}} = 1.2 \times 10^{-9}$$

Note that

$$k_{\mathsf{B}} = 8.617 \times 10^{-5} \mathrm{eV/K}$$

