Thermodynamics of materials

13. Boltzmann Factor

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September 18, 2024

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Boltzmann statistics

- 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.

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

$$\Delta S = S_1 - S_2$$

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.

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

Example

- 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 $T = 298\,\text{K}$, 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 $T = 5772\,\text{K}$, at temperature of the surface of the sun,

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

Note that

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