Physics I

Boltzmann factors

The probability of being in a state with energy ε is proportional to the Boltzmann factor $e^{-\frac{\varepsilon}{k_B T}}$ where $k_B = 1.38\times10^{-23} J/K$

Problem 1.- A paramagnetic atom has two states with energies $E_1 = 0J$, which is the ground state, and $E_2 = 2.87\times10^{-21} J$, which is the excited state.
Calculate the probability of being in the ground state when T = 300 K.

Solution: The Boltzmann factors are:

Ground state: $e^{-E/k_B T} = e^{-0/(1.38\times10^{-23})(300)} = 1$

Excited state: $e^{-E/k_B T} = e^{-2.87\times10^{-21}/(1.38\times10^{-23})(300)} = 1/2$

The probability of being in the ground state is proportional to 1 and the probability of being in the excited state is proportional to ½. But the sum of the two probabilities has to be 100%, so the answer is 67% of being in the ground state (and 33% in the excited state).

Problem 2.- Suppose that an atom has a ground state with energy zero and three excited states with energy ε. The atom is in an environment where the thermal energy $k_B T$ is much larger than ε. Estimate the probability of finding the atom in the ground state.

Solution: If $k_B T$ is much larger that ε, then $e^{-\frac{\varepsilon}{k_B T}}$ is approximately 1, so the probability of being in the ground state is the same as being in any of the three excited states, so the answer is **25%**.

Problem 3.- Which of the following molecules moves fastest in the atmosphere and which is the slowest and why?

Atomic masses: H=1; C=12; N=14; O=16

H_2O CO_2 O_2 N_2

Solution: The fastest in the atmosphere is **H_2O** because it has the lightest mass. The slowest is **CO_2** because it is the heaviest.

Problem 4.- What is the probability of finding the spin of a free electron in its ground state when the magnetic field is B = 1.0 tesla, and the temperature is T = 1.5K?
The product of the magnetic moment times the magnetic field is: $\mu B = 9.3\times10^{-24} J$

Solution: The probabilities are proportional to the Boltzmann factors:

$$P_{ground\ state} = Ce^{\mu B/k_B T}$$

$$P_{first\ excited\ state} = Ce^{-\mu B/k_B T}$$

Since they add to 1: $Ce^{\mu B/k_B T} + Ce^{-\mu B/k_B T} = 1 \rightarrow C = \dfrac{1}{e^{\mu B/k_B T} + e^{-\mu B/k_B T}}$

So, the probability to be in the ground state is:

$$P_{ground\ state} = \frac{e^{\mu B/k_B T}}{e^{\mu B/k_B T} + e^{-\mu B/k_B T}} \quad \text{But: } \frac{\mu B}{k_B T} = \frac{9.3\times10^{-24}\,J}{(1.38\times10^{-23}\,J/K)(1.5K)} = 0.449$$

$$P_{ground\ state} = \frac{e^{0.449}}{e^{0.449} + e^{-0.449}} = \mathbf{0.71}$$

Problem 5.- The Maxwell distribution of gas speeds is given by:

$$f(v) = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{1}{2}\frac{mv^2}{k_B T}}$$

Calculate the most probable speed, which is the speed that has the maximum probability of occurring.

Solution: We find the maximum probability by taking the derivative of the distribution function and equaling it to zero:

$$\frac{df(v)}{dv} = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(2v + v^2\left(-\frac{mv}{k_B T}\right)\right)e^{-\frac{1}{2}\frac{mv^2}{k_B T}} = 0 \rightarrow 2 + v\left(-\frac{mv}{k_B T}\right) = 0$$

So, the speed with the most probability is: $v = \sqrt{\dfrac{2k_B T}{m}}$

Problem 6.- Calculate the ratio of rms speed between SF_6 molecules and He atoms at room temperature if they are diluted enough to treat them as ideal gases.
Atomic mass of S = 32, and F = 19

Solution: The ratio of rms speeds between SF_6 molecules and He atoms at room temperature is:

$$\frac{v_{SF6}}{v_{He}} = \sqrt{\frac{m_{He}}{m_{SF6}}} = \sqrt{\frac{4}{32+6\times19}} = \mathbf{0.166}$$

Problem 7.- Calculate the probability to find a diatomic molecule in its vibrational ground state if the temperature is 300K and the first excited state has an energy of 6.9×10^{-21} J above the ground state. To simplify the problem, consider only two states: the ground state with energy $E_1=0$ and the first excited state.

Solution: The probability is proportional to the Boltzmann factor.
With two levels:

$P_1 = Ce^{-E_1/k_BT}$ and $P_2 = Ce^{-E_2/k_BT}$, but $P_1 + P_2 = 1$, so $C = \dfrac{1}{e^{-E_1/k_BT} + e^{-E_2/k_BT}}$

Then, the probability of being in the ground state is:

$$P_1 = \frac{e^{-E_1/k_BT}}{e^{-E_1/k_BT} + e^{-E_2/k_BT}} = \frac{1}{1+e^{-6.9\times10^{-21}J/(1.38\times10^{-23}J/K\times300K)}} = \mathbf{0.84}$$

Problem 8.- Helium doesn't stay in the atmosphere very long because it has such a light mass that it can easily leave the surface of the Earth. Calculate the average speed (the rms value) of helium at T=300K.

Solution: The rms value of the speed for helium at T=300K.

$$v_{rms} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3(1.38\times10^{-23})(300)}{4\times1.66\times10^{-27}}} = \mathbf{1{,}360\ m/s}$$

Problem 8a.- Calculate the rms average speed of the amino acid Glycine in the gas phase at 37ºC knowing that its mass is 75 amu and it can be treated as an ideal gas.
1amu=1.66×10^{-27} kg

Solution:

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_BT \rightarrow v_{rms} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\times1.38\times10^{-23}\times(37+273)}{75\times1.66\times10^{-27}}} = \mathbf{321\ m/s}$$

Problem 8b.- In principle, can we separate N_2 from O_2 by diffusion? What is the ratio of speeds of these two molecules at room temperature?

Problem 9.- Calculate the probability that an electron will be in the conduction band of silicon, whose energy is 1.12 eV higher than the valence band. Take T=300K and to simplify the problem consider only two states: the ground state with energy $E_1=0$ and the first excited state with $E_2=1.12$eV.

1 eV=1.6×10^{-19} J

Solution: To figure the probability we use the Boltzmann factors:

$$p = \frac{e^{-E_2/k_BT}}{e^{-E_1/k_BT} + e^{-E_2/k_BT}} = \frac{e^{-E_2/k_BT}}{1+e^{-E_2/k_BT}} \approx e^{-E_2/k_BT} = e^{-1.12\times1.6\times10^{-19}/1.38\times10^{-23}\times300} = \mathbf{1.59\times10^{-19}}$$