BOLTZMANN EQUATION FOR ENERGY LEVELS IN STELLAR ATMOSPHERES

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Reference: Carroll, Bradley W. & Ostlie, Dale A. (2007), *An Introduction to Modern Astrophysics*, 2nd Edition; Pearson Education - Chapter 8, Problems 8.5 - 8.6.

In a stellar atmosphere, the distribution of velocities of the atoms follows the Maxwell-Boltzmann distribution

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} 4\pi v^2 dv \tag{1}$$

Here, n is the number density of gas molecules, each of mass m, k is Boltzmann's constant and T is the temperature. As a result of collisions between atoms, energy is exchanged which results in the electrons in some atoms being bumped up to one of the excited states of those atoms. In thermal equilibrium, the ratio of probabilities (and hence, for large numbers of atoms, the ratio of the numbers of atoms) for an atom being in quantum states s_a and s_b is given by the Boltzmann equation

$$\frac{P(s_b)}{P(s_a)} = \frac{N_b}{N_a} = \frac{g_b e^{-E_b/kT}}{g_a e^{-E_a/kT}} = \frac{g_b}{g_a} e^{-(E_b - E_a)/kT} \tag{2}$$

where $g_{a,b}$ are the degeneracies of states $s_{a,b}$, that is, the number of different quantum states that have the same energy.

For the hydrogen atom, the degeneracy of the state with principal quantum number n is given by $2n^2$.

Example 1. We can use the Boltzmann equation to work out the relative numbers of atoms in various excited states at a given temperature if we know the energy levels. For hydrogen, the ground state is $E_1 = -13.6$ eV, and due to the Bohr formula, the energy of excited state n is $1/n^2$ times the ground state energy.

Let's find the temperature at which the number of hydrogen atoms in the first excited state is 1% of the atoms in the ground state. The energy of the $n = 2$ state is $E_2 = -\frac{13.6}{4}$ eV $= -3.4$ eV. The degeneracies of the first two states are $g_1 = 2$ and $g_2 = 8$, so we get

$$\frac{N_2}{N_1} = 0.01 = \frac{8}{2}e^{-10.2/kT} \tag{3}$$

$$kT = -\frac{10.2}{\ln 0.0025} = 1.7 \text{ eV} \tag{4}$$

Using the approximate value of $kT = \frac{1}{40}$ eV for room temperature $T = 300$ K, this gives a temperature of around $T = 300 \times 1.7 \times 40 = 20,400$ K.

If N_2 is 10% of N_1, we have

$$\frac{N_2}{N_1} = 0.1 = \frac{8}{2}e^{-10.2/kT} \tag{5}$$

$$kT = -\frac{10.2}{\ln 0.025} = 2.765 \text{ eV} \tag{6}$$

The corresponding temperature is $T = 300 \times 2.765 \times 40 = 33,180$ K.

Example 2. At what temperature are there equal numbers of hydrogen atoms in the ground state $n = 1$ and the second excited state $n = 3$? The required energy is $E_3 = -13.6/3^2 = -1.5$ eV so we get

$$\frac{N_3}{N_1} = 1 = \frac{18}{2}e^{-12.1/kT} \tag{7}$$

$$kT = -\frac{12.1}{\ln 0.111} = 5.51 \text{ eV} \tag{8}$$

$$T = 5.51 \times 40 \times 300 = 66,000 \text{ K} \tag{9}$$

Somewhat surprisingly, this temperature is lower than the temperature of 85,400 K at which equal numbers of atoms are in the $n = 1$ and $n = 2$ states. This appears to be due to the higher degeneracy of the $n = 3$ state (18 degenerate states for $n = 3$ as opposed to 8 for $n = 2$). At a temperature of 85,400 K, where $N_1 = N_2$, we can find N_3 as follows. At this temperature, $kT = 7.12$ eV

$$N_3 = N_1\frac{18}{2}e^{-12.1/7.12} \tag{10}$$

$$= 1.64N_1 \tag{11}$$

As the temperature increases, the exponent $-(E_b - E_a)/kT \to 0$ for all energy levels, so the exponential factor tends to 1. Given that the ratio of degeneracies $g_n = 2n^2$ increases with larger n, the Boltzmann equation predicts that the higher energy levels will become increasingly populated, as we might expect, with level n having n^2 as many atoms as the ground state. In reality, however, we'd expect most atoms to become ionized at extremely high temperatures, so the Boltzmann equation probably breaks down in this case.

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