The Boltzmann Equation

gas:
$$n = g \left(\frac{2\pi m kT}{h^2}\right)^{3/2} e^{\mu/kT} e^{-\varepsilon_0/kT}$$

Ideal

Consider two species of particles: atoms in different energy levels that can be excited or de-excited via photons.

e.g.,
$$H_1 + \gamma \rightarrow H_2$$
 $1\mu_{H_1} + 0 = 1\mu_{H_2}$
$$\frac{n_1}{n_2} = \frac{g_1 (2\pi m kT/h^2)^{3/2} e^{\lambda_1/kT} e^{-\varepsilon_1/kT}}{g_2 (2\pi m kT/h^2)^{3/2} e^{\mu_2/kT} e^{-\varepsilon_2/kT}} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_2 e^{-\varepsilon_2/kT}}$$
$$\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{-(\varepsilon_1 - \varepsilon_2)/kT}$$

 g_2

The Boltzmann Equation

Total number of atoms:
$$n_{tot} = \sum_{i} n_{i}$$

 $\frac{n_{\text{tot}}}{n_i} = \frac{n_1}{n_i} + \frac{n_2}{n_i} + \cdots = \frac{g_1}{g_i} e^{-\varepsilon_1/kT} e^{\varepsilon_i/kT} + \frac{g_2}{g_i} e^{-\varepsilon_2/kT} e^{\varepsilon_i/kT} + \cdots$

$$=\frac{1}{g_i}e^{\varepsilon_i/kT}\left(g_1e^{-\varepsilon_1/kT}+g_2e^{-\varepsilon_2/kT}+\cdots\right) =\frac{1}{g_ie^{-\varepsilon_i/kT}}\sum_j g_je^{-\varepsilon_j/kT}$$

$$\frac{n_i}{n_{\rm tot}} = \frac{g_i}{G} e^{-\varepsilon_i/kT}$$

Partition function:
$$G = \sum_{j} g_{j} e^{-\varepsilon_{j}/kT}$$

Like an effective statistical weight for all states

Consider an atomic gas that is partly ionized $\mathcal{E}_{+} = \chi$ e.g., $|H^+ + e^- \leftrightarrow H^0 + \gamma| = 1\mu^0 = 1\mu^0$ $\mathcal{E}_0 = 0$ • charged ions in ground state $n^+ = g^+ \left(\frac{2\pi m_p kT}{h^2}\right)^{3/2} e^{\mu^+/kT} e^{-\chi/kT}$ $n^{-} = g^{-} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{\mu^{-}/kT}$ free electrons $n^{0} = g^{0} \left(\frac{2\pi m_{p} kT}{h^{2}} \right)^{3/2} e^{\mu^{0}/kT}$ neutral ions in ground state $\frac{n^{+}n^{-}}{n^{0}} = \frac{g^{+}g^{-}}{g^{0}} \left(\frac{2\pi m_{e}kT}{h^{2}}\right)^{3/2} e^{-\chi/kT}$ Combine to eliminate chemical potentials

$$\frac{n^{+}n^{-}}{n^{0}} = \frac{g^{+}g^{-}}{g^{0}} \left(\frac{2\pi m_{e}kT}{h^{2}}\right)^{3/2} e^{-\chi/kT}$$

This is only for atoms in the ground state.

In general, we have neutral and ionized atoms in multiple states Use Boltzmann to generalize to all states of a given atom







$$\frac{n^{+}n_{e}}{n^{0}} = \frac{2G^{+}}{G^{0}} \left(\frac{2\pi m_{e}kT}{h^{2}}\right)^{3/2} e^{-\chi/kT}$$

Example: pure H



$$n^{+} = yn_{I}$$

$$n^{0} = (1 - y)n_{I} \begin{cases} \frac{n^{+}n_{e}}{n^{0}} = \frac{yn_{I} \cdot yn_{I}}{(1 - y)n_{I}} = \frac{y^{2}}{1 - y}n_{I} \end{cases}$$

$$n_{e} = yn_{I}$$

$$\frac{y^{2}}{1 - y} = \frac{1}{n_{I}} \left(\frac{2\pi m_{e}kT}{h^{2}}\right)^{3/2} e^{-\chi/kT} \qquad n_{I} = N_{A}\rho$$

 $\frac{y^2}{1-y} = \frac{4 \times 10^{-9} \,\text{g cm}^{-3}}{\rho} T^{3/2} e^{-1.578 \times 10^5/T}$ 50% ionized at T=10⁴K for low densities

Example: Balmer line strength Strength of Balmer lines depend on fraction of H gas that is in the n=2 excited state.

13.6eV
$$n = \infty$$

 $n = 3$
 $10.2eV$ $n = 2$

We want $\frac{n_2^0}{n_I}$ 0 (n=1)Boltzmann gives us $\frac{n_2^0}{n^0} = \frac{g_2^0}{G^0} e^{-\varepsilon_2/kT}$

$$\frac{n_{2}^{0}}{n_{I}} = \frac{n_{2}^{0}}{n_{I}} \frac{n^{0}}{n_{I}}$$

$$\frac{n_{2}^{0}}{n_{I}} = (1-y)\frac{g_{2}^{0}}{G^{0}}e^{-\varepsilon_{2}/kT}$$

$$g_{2}^{0} = 8$$

$$G^{0} = \sum_{i} g_{i}e^{-\varepsilon_{i}/kT} \approx 2$$

$$\varepsilon_{2} = 10.2 \text{ eV}$$

$$\frac{n_2^0}{n^0} = (1 - y) \frac{g_2^0}{G^0} e^{-\varepsilon_2/kT}$$

$$\frac{y^2}{1-y} = \frac{1}{n} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-\chi/kT}$$



A different way to write the Saha equation

$$\frac{n^{+}n_{e}}{n^{0}} = \frac{2G^{+}}{G^{0}} \left(\frac{2\pi m_{e}kT}{h^{2}}\right)^{3/2} e^{-\chi/kT}$$

$$\log\left(\frac{n^{+}n_{e}}{n^{0}}\right) = \log\left(\frac{2G^{+}}{G^{0}}\right) + \frac{3}{2}\log\left(\frac{2\pi m_{e}kT}{h^{2}}\right) + \log\left(e^{-\chi/kT}\right)$$
$$\log\left(\frac{n^{+}}{n^{0}}\right) + \log n_{e} = \log\left(\frac{2G^{+}}{G^{0}}\right) + \frac{3}{2}\log\left(\frac{2\pi m_{e}k}{h^{2}}\right) + \frac{3}{2}\log T - \ln 10\frac{\chi}{kT}$$

$$P_e = n_e kT \quad \rightarrow \log n_e = \log P_e - \log k - \log T$$

$$\log\left(\frac{n^{+}}{n^{0}}\right) = \log\left(\frac{2G^{+}}{G^{0}}\right) + \frac{5}{2}\log T - \log P_{e} - \frac{5040\chi}{T} - 0.48$$

The Saha equation works best at moderate densities

- At very low densities (e.g., corona), we must worry about whether LTE applies.
- At very high densities, atoms are not isolated.



Overlap of potentials of neighboring atoms lowers the effective ionization energy, which leads to greater ionization than Saha predicts.

For density *n* and separation *a* : $n = \left(\frac{4}{3}\pi a^3\right)^{-1}$

set *a* = radius of first Bohr orbit of *H* = 0.5×10^{-8} cm $\rightarrow \rho \sim 3$ g cm⁻³

Above this density, even the ground state is affected and all H is ionized.

 For ions of charge Z, the ratio of electrostatic energy to thermal energy is a measure of whether Coulomb effects affect the ideal-ness of an ideal gas.

$$\Gamma_C = \frac{Z^2 e^2/a}{kT} \qquad \qquad \Gamma_C = 1 \rightarrow \rho = 85 \text{ g cm}^{-3} \left(\frac{T}{10^6 K}\right)^3$$

Important in very low mass stars

Equation of State

For pure H

- ideal gas vs. radiation $\rho = 1.5 \times 10^{-23} T^3$
- degenerate vs. not $\rho = 6 \times 10^{-9} T^{3/2}$
- neutral vs. ionized $\rho = 8 \times 10^{-9} T^{3/2} e^{-1.58 \times 10^5/T}$
- pressure ionized $\rho \approx 1$
- Coulomb effects $\rho = 8.5 \times 10^{-17} T^3$
- crystalline structure $\rho = 4.2 \times 10^{-10} T^3$

