

Boltzmann law

In general population of different energy levels depends upon detailed processes leading to population / depopulation.

Easy in thermal equilibrium – depends only upon temperature T .
Relative populations are:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(\varepsilon_2 - \varepsilon_1)/kT}.$$

Taking the ground state as a zero point, population of a level with energy ε_i and statistical weight g_i is,

$$N_i = \frac{N}{U} g_i e^{-\varepsilon_i/kT}$$

where N is the total population (number per unit volume) and U is the *partition function*.

Since,

$$N = \sum N_i$$

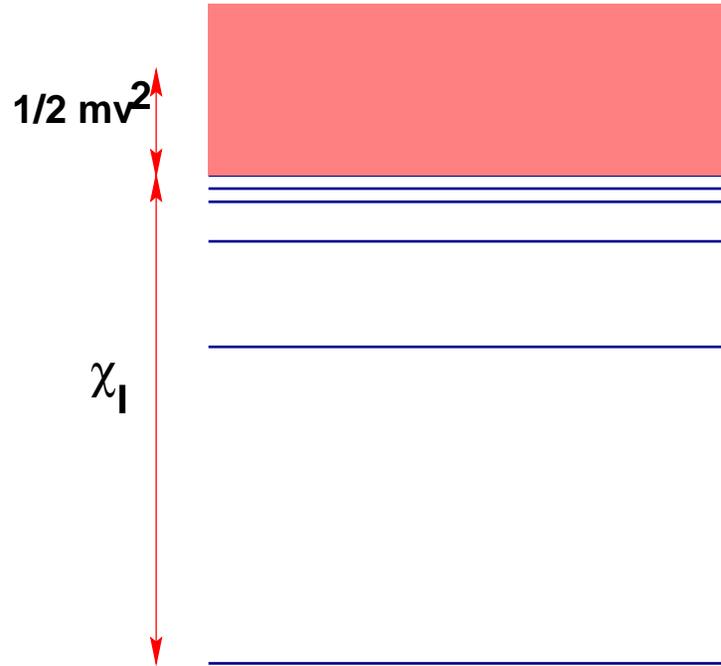
we must have,

$$U = \sum g_i e^{-\varepsilon_i/kT}.$$

At low temperatures only the first term is significant and U equals the statistical weight of the ground state.

The Saha equation

The Saha equation gives the distribution of atoms in different stages of ionization. Simplest case: a neutral atom and its first stage of ionization.



Consider the ground state of the neutral atom, and the ground state of the ion with the free electron having velocity v . Energy difference is,

$$\Delta\mathcal{E} = \chi_I + \frac{1}{2}m_e v^2$$

where χ_I is the ionization potential. Boltzmann law suggests,

$$\frac{dN_0^+(v)}{N_0} = \frac{g}{g_0} \exp \left[-\frac{(\chi_I + 1/2 m_e v^2)}{kT} \right],$$

Where:

- $dN_0^+(v)$ is the differential number of ions in the ground state with the free electron having velocity between v and $v + dv$.
- N_0 is number of atoms in ground level.
- g_0 is the statistical weight of the atom in the ground state.
- g is the product of the statistical weight of the ion in its ground state g_0^+ , and the differential statistical weight of the electron g_e .
ie

$$g = g_0^+ g_e$$

For the electron, with two spin states,

$$g_e = \frac{2dx_1dx_2dx_3dp_1dp_2dp_3}{h^3}.$$

The volume $dx_1dx_2dx_3$ contains one electron, so $dx_1dx_2dx_3 = 1/n_e$, where n_e is the electron density. Since the electrons have an isotropic velocity distribution,

$$dp_1dp_2dp_3 = 4\pi m_e^3 v^2 dv$$

Substituting,

$$\frac{dN_0^+(v)}{N_0} = \frac{8\pi m_e^3}{h^3} \frac{g_0^+}{N_e g_0} \exp \left[-\frac{(\chi_I + 1/2 m_e v^2)}{kT} \right] v^2 dv.$$

Integrating over all possible v ,

$$\frac{N_0^+ N_e}{N_0} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \frac{2g_0^+}{g_0} e^{-\chi_I/kT}$$

Boltzmann laws give,

$$\begin{aligned} \frac{N_0}{N} &= \frac{g_0}{U(T)} \\ \frac{N_0^+}{N^+} &= \frac{g_0^+}{U^+(T)}. \end{aligned}$$

Substituting these gives us *Saha's equation*,

$$\frac{N^+ N_e}{N} = \frac{2U^+(T)}{U(T)} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\chi_I/kT},$$

where N and N^+ are the number densities of neutral and first ionized atoms, and U and U^+ are the corresponding partition functions.

Saha's equation for *any* two neighbouring states of ionization is just the same, replace N by N_j , N^+ by N_{j+1} etc.

Ionization of hydrogen

To apply to hydrogen, need the partition functions. Take:

- $U = 2$ (ground state value)
- $U^+ = 1$

For pure hydrogen, electrical neutrality and conservation of nucleon number imply,

$$n_e = n^+$$

and,

$$n = n^+ + n^0$$

where n is now the total number density (neutral + ionized atoms).

Define the degree of ionization y by,

$$y = \frac{n^+}{n}.$$

The Saha equation can then be written,

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

Limits,

- $T \rightarrow \infty, y \rightarrow 1$
- $T \rightarrow 0, y \rightarrow 0$

Numerically,

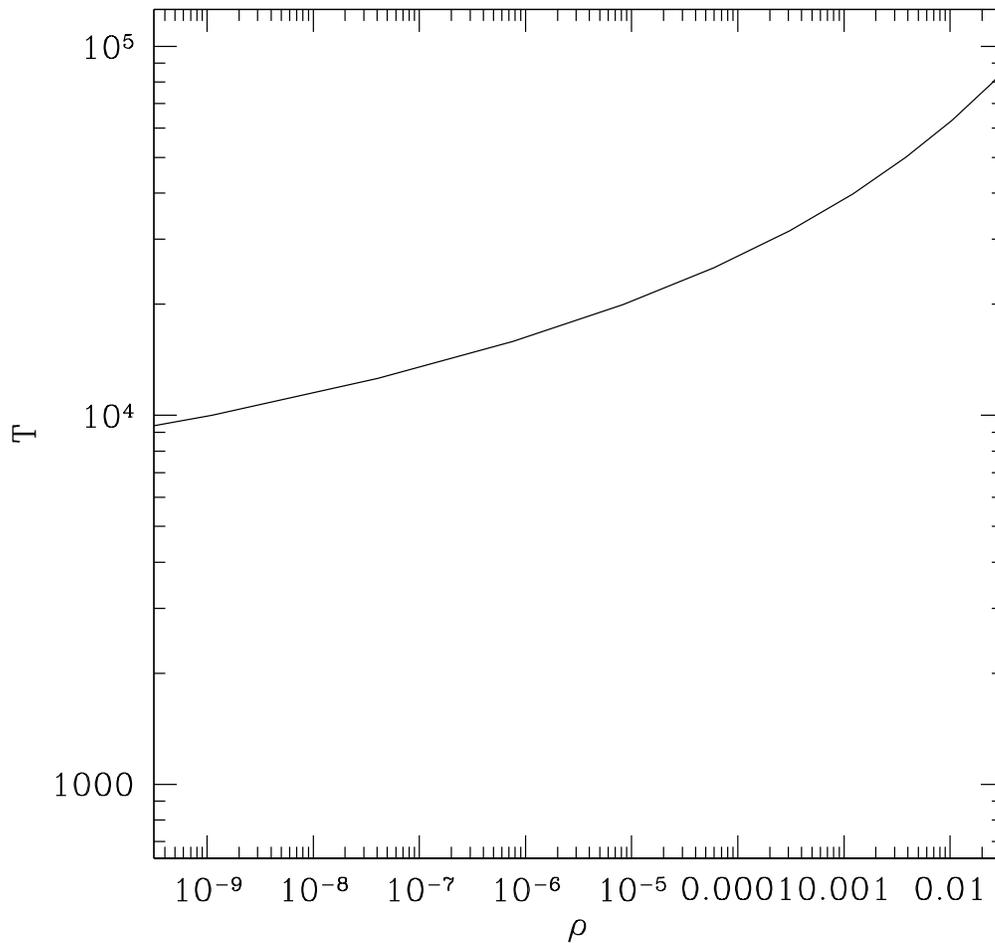
$$n = \rho N_A$$

for pure hydrogen so,

$$\frac{y^2}{1-y} = \frac{4 \times 10^{-9} \text{ g cm}^{-3}}{\rho} T^{3/2} e^{-1.578 \times 10^5/T}$$

Application to hydrogen

The Saha equation predicts that pure hydrogen is 50% ionized at $T \simeq 10^4$ K for low density, with the critical T rising slowly with density.

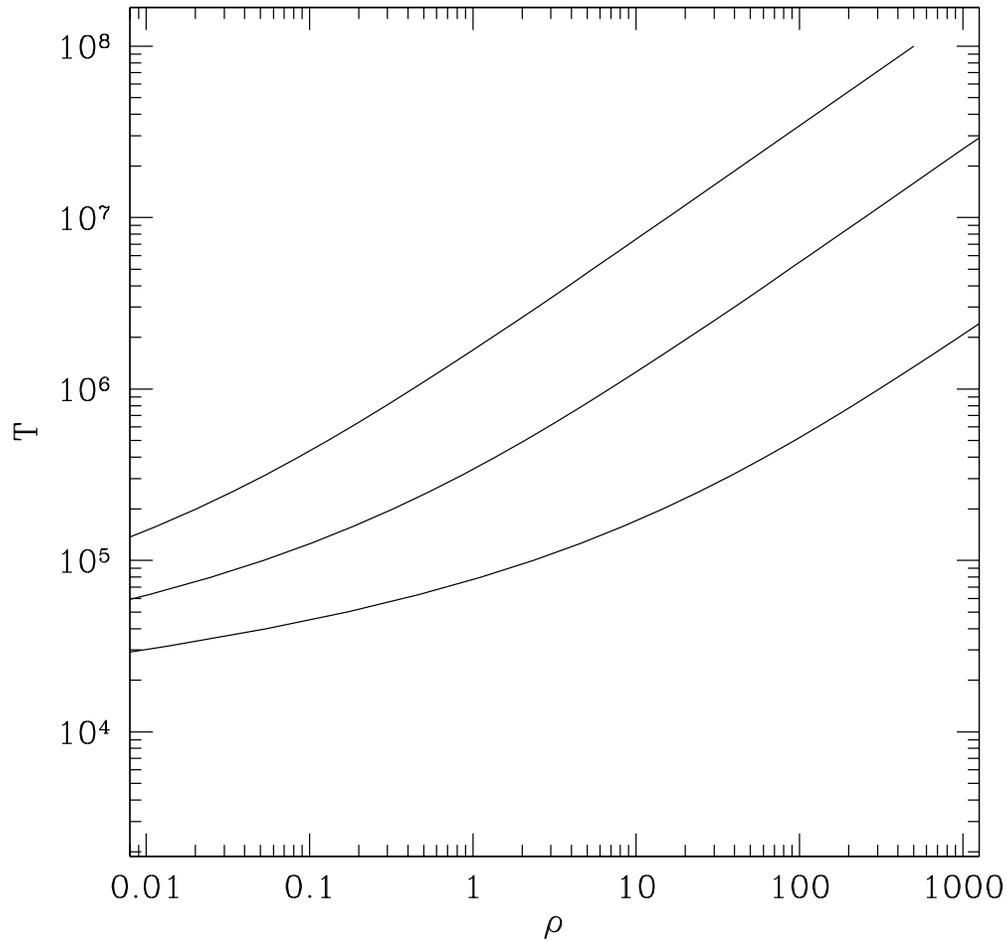


Note: pure H means exactly that. Even a small amount of metals can be important because they can be ionized easily.

Limits to the Saha equation

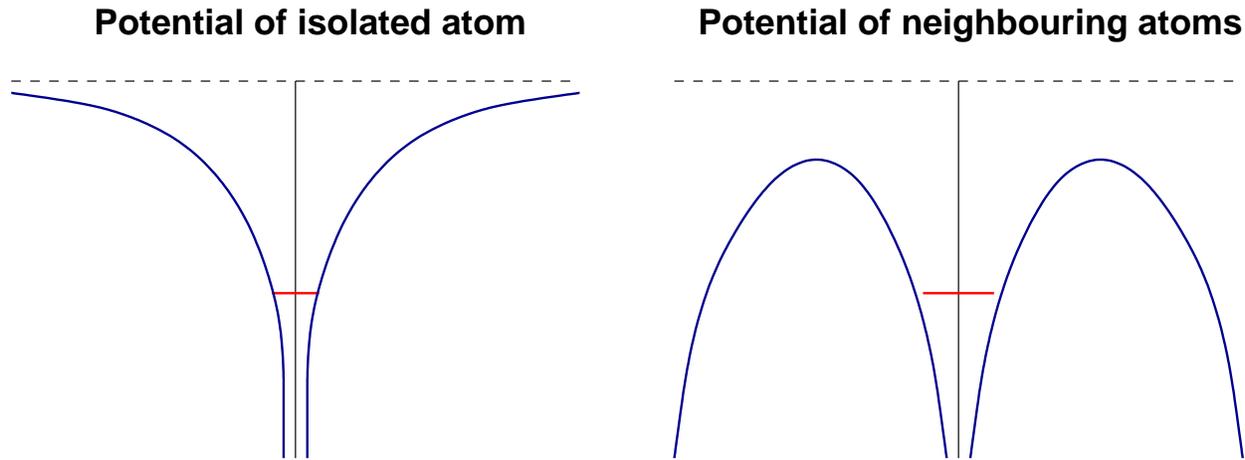
Saha formula works best at modest densities. At very low density (e.g. in the corona) need to worry whether local thermodynamic equilibrium conditions apply.

At high density, Saha equation predicts that pure hydrogen is 10%, 50%, 90% ionized at temperatures given by:



Pressure ionization

Problem arises because the derivation of the Saha equation assumes that the atoms are isolated – not true at high densities. Schematically:



Overlap of the potentials of neighbouring ions lowers the effective ionization energy \rightarrow greater degree of ionization than Saha predicts.

Estimate of the density required for *pressure ionization*:

For ion density n_I , characteristic separation a is,

$$\frac{4}{3}\pi a^3 = \frac{1}{n_I}.$$

Set this equal to the radius of the first Bohr orbit of hydrogen, 0.5×10^{-8} cm to give,

$$\rho \sim 3 \text{ g cm}^{-3}$$

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

In practice, OK to assume full ionization at depths in the star where Saha equation predicts decreasing ionization fraction.

Coulomb effects

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

$$\Gamma_c \equiv \frac{Z^2 e^2}{akT}$$

Using previous definition of a , $\Gamma_c = 1$ for hydrogen at,

$$\rho = 85 \left(\frac{T}{10^6 \text{ K}} \right)^3 \text{ g cm}^{-3}.$$

Important for very low mass stars. Also, for large $\Gamma_c \sim 170$ crystallization may occur – possibly relevant to cool white dwarfs.