

Saha's Equation and the Partition Function

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Abstract

The Saha equation is usually derived using an argument involving one of the classical thermodynamic functions, the Gibbs' free energy. Sometimes dynamical arguments are used. Since the Saha result is a statistical relation, it would be desirable to have less roundabout methods for its derivation. Here the Saha equation is derived directly from the partition function.

The dissociation interaction



is encountered under many conditions:

Process	Equation	ΔE (eV)
Molecular dissociation:	$H_2 \leftrightarrow 2H$	-4.476
Atomic ionization:	$H \leftrightarrow p^+ + e^-$	-13.597

The dissociation process is described by the Saha equation.

To motivate the result that follows, we first begin with a very simple example. Suppose we start with three "molecules" of type AB . Each dissociates into two different "atoms" A and B . The partition function, counting all possible states weighted by their Boltzmann factors, is

$$Z_{Tot} = \frac{Z_{AB}^3}{3!} + \frac{Z_{AB}^2}{2!} \frac{Z_A^1}{1!} \frac{Z_B^1}{1!} + \frac{Z_{AB}^1}{1!} \frac{Z_A^2}{2!} \frac{Z_B^2}{2!} + \frac{Z_A^3}{3!} \frac{Z_B^3}{3!} \quad (2)$$

In this expression $Z_A = V(2\pi M_A kT/h^2)^{3/2} Z_a(int)$. The first factor comes from an integral over the phase space of the center of mass coordinates of the particle. The second factor, $Z_a(int)$, is the partition function counting only the *internal* states of A . Similarly for B and the combined particle AB . Each term in Eq. (2) accounts for one of the possibilities suggested by Eq. (1). The part $\frac{Z_{AB}^3}{3!}$ is the relative probability that exactly 3 AB molecules are present. The molecules are indistinguishable, hence the factor of $\frac{1}{3!}$. The second term, $\frac{Z_{AB}^2}{2!} \frac{Z_A^1}{1!} \frac{Z_B^1}{1!}$, is the relative probability that two molecules AB are present with one "atom" each of A and B . And so it goes. The absolute probabilities are obtained by

normalizing each of these (four) terms with their sum, Z_{Tot} . It will not be necessary to do this normalization.

When lots of atoms AB and their dissociation products are present, the total partition function is a simple generalization of that given in Eq.(2):

$$Z_{Tot} = \sum \frac{Z_{AB}^{N_{AB}}}{N_{AB}!} \frac{Z_A^{N_A}}{N_A!} \frac{Z_B^{N_B}}{N_B!} \quad (3)$$

The sum extends over all allowed values of the integers N_{AB} , N_A and N_B . The integers are not free to vary arbitrarily: if N_{AB} decreases by one, N_A and N_B must increase by one.

Instead of trying to carry out this sum, it is simpler just to look for the most likely state: the state of largest probability. Roughly but accurately, as the integer N_{AB} decreases by integer steps and the two integers N_A and N_B each increase by integer steps, the relative probabilities will first rise, then reach a maximum, then finally decrease. At the largest likelihood, two successive relative probabilities will be approximately equal. We can represent this condition as

$$\frac{Z_{AB}^{N_{AB}}}{N_{AB}!} \frac{Z_A^{N_A}}{N_A!} \frac{Z_B^{N_B}}{N_B!} = \frac{Z_{AB}^{N_{AB}-1}}{(N_{AB}-1)!} \frac{Z_A^{N_A+1}}{(N_A+1)!} \frac{Z_B^{N_B+1}}{(N_B+1)!} \quad (4)$$

This is easily rewritten as

$$\frac{Z_{AB}}{N_{AB}} = \frac{Z_A}{N_A+1} \frac{Z_B}{N_B+1} \quad (5)$$

For large numbers of particles there is little difference between N_A+1 and N_A , so we can neglect the $+1$'s in the denominator on the right hand side. Now substituting the expressions for the three individual partition functions Z_{AB} , Z_A and Z_B into this expression, we find

$$\frac{V(2\pi M_{AB}kT/h^2)^{3/2} Z_{ab}(int)}{N_{AB}} = \frac{V(2\pi M_AkT/h^2)^{3/2} Z_a(int)}{N_A} \frac{V(2\pi M_BkT/h^2)^{3/2} Z_b(int)}{N_B} \quad (6)$$

In each of these three factors there is a ratio of $V/N_* = 1/(N_*/V) = 1/[n_*]$. Here $[n_*]$ is the density of particles of type $*$. We measure this in number of particles per cm^3 . By unwinding these factors carefully, we find

$$\frac{[n_A][n_B]}{[n_{AB}]} = \left(\frac{2\pi(M_A M_B / M_{AB})kT}{h^2} \right)^{3/2} \frac{Z(int)_a Z(int)_b}{Z(int)_{ab}} \quad (7)$$

We now turn this into a computationally useful expression. We assume that AB is bound by an energy ΔE which is negative (-13.6 for the hydrogen atom and -4.476 for the hydrogen molecule). We assume the molecule AB has no internal structure and only the single bound state at ΔE , so $Z(int)_a = e^{-\beta\Delta E}$. We further assume that neither A nor B has any internal structure, so that $Z(int)_a = 1$, $Z(int)_b = 1$. Next, we introduce a *reaction coordinate* x that describes quantitatively how far the reaction proceeds in some direction (by

convention, to the right). In terms of this coordinate, if the initial concentration of molecules AB at low temperature is n_0 , at finite temperature T , $[n_{AB}] = (1-x)n_0$ while $n_A = n_B = xn_0$. Taking logs (to base e) of both sides of Eq.(7) we find

$$\log\left(\frac{x^2}{1-x}\right) = \beta\Delta E - \frac{3}{2}\log(-\beta\Delta E) + \frac{3}{2}\log\left(\frac{2\pi(M_A M_B/M_{AB})(-\Delta E)}{n_0^{2/3}h^2}\right) \quad (8)$$

If the masses are measured in units of the proton mass, energies are measured in electron volts, and densities are measured in ‘‘Avogardos per cm^3 ’’, this expression becomes

$$\log\left(\frac{x^2}{1-x}\right) = \beta\Delta E - \frac{3}{2}\log(-\beta\Delta E) + 5.9769 + \frac{3}{2}\log(M/M_p) + \frac{3}{2}\log(|\Delta E|/(1\text{eV})) - \log(n/n_0) \quad (9)$$

Application 1: ‘‘Recombination’’

As the universe expanded and cooled after the Big Bang, the temperature and the particle density decreased to a point where it was entropically feasible for charged free protons and oppositely charged free electrons to combine to form electrically neutral hydrogen atoms:



This occurred about 380,000Y after the Big Bang. At this time the temperature was about 3000 °K and the baryon density was about 1.2×10^2 protons/ cm^3 , so that $n/n_0 = 0.2 \times 10^{-21}$. We use $M_p M_e/M_H = M_e = 1/1836$, measured in units of proton mass. The reaction coordinate x , as a function of temperature, is derived from Eq.(9) and plotted in Fig. (1).

Technical Details: These details can be skipped on first reading. Both the electron and the proton have spin $\frac{1}{2}$, so each momentum state is two-fold degenerate. As a result, both the electron and the proton partition functions should be multiplied by a factor of 2. Countering that, the hydrogen atom 1s ground state is four-fold degenerate (both the proton and electron can have spin up or spin down), so its partition function should be multiplied by a factor of 4. The ratio $2^2/4$ leaves Eq. (9) unchanged.

A more serious problem concerns the internal structure of the hydrogen atom. It would seem that the appropriate internal partition function, consisting of the sum of the Boltzmann factors over all possible bound states, is

$$Z_H(int) = \sum_{\text{Bound States}} e^{-\beta E_n} \rightarrow \sum_{n=1}^{\infty} 4 \times n^2 e^{-\beta E_g/n^2} \rightarrow ‘‘\infty’’$$

where $E_g = -13.58$ eV. This sum diverges. We have kept only the first term in this sum in Eq. (9), which is very small except for very high temperatures.

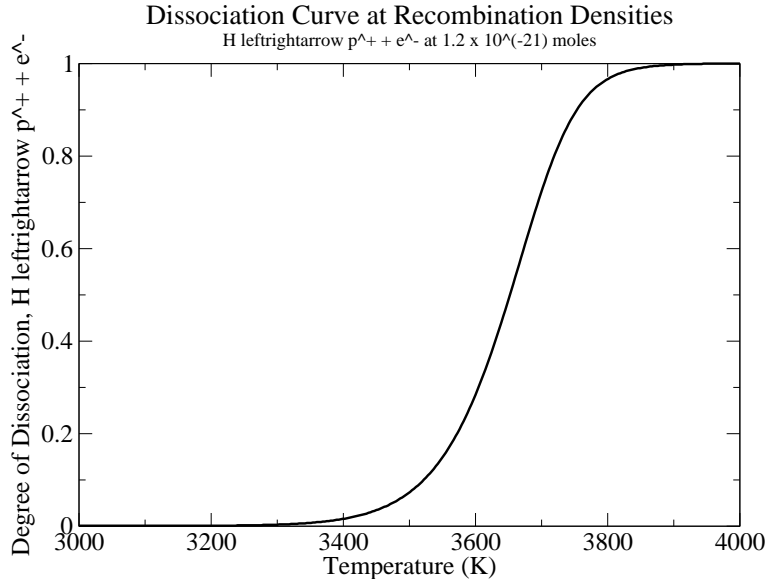


Figure 1: Reaction coordinate x as a function of temperature at about 380,000 ABB when the baryon density is about 1.2×10^2 protons per cm^3 .

What justifies this gross approximation? We claim that the Boltzmann factors for the excited hydrogenic states should not be considered on the grounds that these states are not in thermal equilibrium with the surroundings. To justify this claim we point out that population inversion of the higher states, leading to observed maser radiation, is not possible in thermal equilibrium.

Application 2: Molecular Dissociation

At the surface of some stars the molecular to atomic dissociation



takes place. Molecular hydrogen is bound by 4.476 eV at 0° K. We introduce a reaction coordinate x as above. If the concentration of H_2 at very low temperatures is n_0 , then at higher temperatures $[n_{H_2}] = (1 - x)n_0$ and $[n_H] = 2xn_0$. The left-hand side of Eq.(9) is $\log(\frac{(2x)^2}{1-x})$ while the right hand side differs in the values of the parameters ΔE and n_0 . If we choose $n_0 = \frac{1}{2}$ Avogardo, the dissociation curve is as shown in Fig. 2.

The molecular dissociation shown in Fig. (2) occurs at a slightly higher temperature (by a factor of 4) than the recombination, or atomic ionization that is shown in Fig. (1). This is due to the vastly different densities that have been assumed for the two cases. In the first case the density is about 10^2 protons / cm^3 while for the second case it is larger by 21 orders of magnitude.

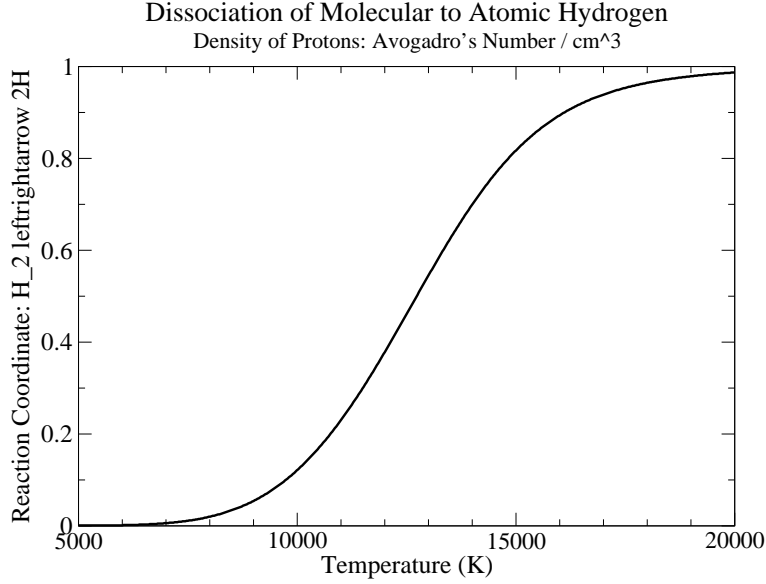


Figure 2: Reaction coordinate x as a function of temperature for dissociation of molecular into atomic hydrogen at the surface of a star where the density is 6.024×10^{23} protons per cm^3 .

Application 3: Dissociation - Ionization

A gas of molecular hydrogen at fairly low temperature will dissociate into atomic hydrogen as the temperature increases, and the atomic hydrogen will dissociate (“ionize”) as the temperature continues to increase. The two processes can be described by the Saha equation. We formulate this double dissociation process in terms of Boltzmann factors and partition functions.

The partition function describing all possible states is

$$Z = \sum \frac{Z_{H_2}^{N_{H_2}}}{N_{H_2}!} \frac{Z_H^{N_H}}{N_H!} \frac{Z_{p^+}^{N_{p^+}}}{N_{p^+}!} \frac{Z_{e^-}^{N_{e^-}}}{N_{e^-}!} \quad (12)$$

The contribution to this sum with the largest weight is searched for in *two* different directions, corresponding to the two independent reactions. These are described by the *stoichiometric coefficients* ν_i :

Reaction Coord.	H_2	H	p^+	e^-
x	-1	+2	0	0
y	0	-1	+1	+1

The equilibrium conditions are

$$\prod_{i=1} \left(\frac{Z_i}{N_i} \right)^{\nu_i} = 1 \quad \text{for each reaction} \quad (13)$$

When we unwind the two expressions represented by Eq. (13) in terms of the stoichiometric coefficients ν_i , the factors $(2\pi mkT/h)^{3/2}$, and the internal partition functions, we find

$$\text{Rx 1 : } \quad \frac{[n_H]^2}{[n_{H_2}]} = \frac{1}{e^{-\beta E_1}} \left(\frac{2\pi(M_H^2/M_{H_2})kT}{h^2} \right)^{3/2} \quad (14)$$

$$\text{Rx 2 : } \quad \frac{[n_{p^+}][n_{e^-}]}{[n_H]} = \frac{1}{e^{-\beta E_2}} \left(\frac{2\pi(M_{p^+}M_{e^-}/M_H)kT}{h^2} \right)^{3/2} \quad (15)$$

There are two reactions and four reactants. The four concentrations can be expressed in terms of $2 = 4 - 2$ reaction coordinates. We begin with an electrically neutral gas of hydrogen molecules at low temperature, with a concentration of n_0 molecules/cm³. at any finite temperature, $[n_{H_2}] = (1-x)n_0$, $[n_H] = 2(x-y)n_0$, and $[n_{p^+}] = [n_{e^-}] = 2yn_0$. Two two equations that define the values of the two reaction coordinates are now

$$1 : \log \frac{[2(x-y)]^2}{1-x} = \beta E_1 - \frac{3}{2} \log(\beta |E_1|) + \frac{3}{2} \log \left(\frac{2\pi(\frac{1}{2}M_H)|E_1|}{n_0^{2/3}h^2} \right) \quad (16)$$

$$2 : \log \frac{(2y)^2}{2(x-y)} = \beta E_2 - \frac{3}{2} \log(\beta |E_2|) + \frac{3}{2} \log \left(\frac{2\pi M_e |E_2|}{n_0^{2/3}h^2} \right) \quad (17)$$

$$(18)$$

This pair of coupled nonlinear equations is certainly formidable looking. However, as long as the two dissociation energies E_1 and E_2 are “very different” the results are easy to describe. Very different means the transition ranges from $x \simeq 0 \rightarrow x \simeq 1$ and $y \simeq 0 \rightarrow y \simeq 1$ are both narrower than the energy difference $|E_1 - E_2|$. In this case, as a function of increasing temperature x rises from 0 to 1 while y remains 0. After a further increase of temperature y rises from 0 to 1 while x remains 1. The temperatures at which the two transitions take place can be computed as if only a single process were taking place. Note that we cannot use Figs. (2) and (1) in series because they were computed under vastly different density conditions. Note also that a density change of 10^{10} corresponds to a temperature change by a factor of only about $23 \simeq 10^{1.37}$.