Saha's Equation: Dissociation and Ionization of Hydrogen

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ABSTRACT

In this report, we use Saha's equation to find the equilibrium concentrations of molecular hydrogen H_2, atomic hydrogen H and ionized hydrogen $p^+ + e^-$ on the surface of a star. We will look at temperatures ranging from 0K to 40000K and we will also explore several different densities for the star's surface. Afterwards, we will use the same method to look at the behavior of an organic compound that goes through a similar reaction, called the decarboxylation of acetoacetic acid. We will scale the density and the temperatures accordingly.

1. INTRODUCTION

A. The Saha Equation

The Saha equation is a formula that allows us to see the relationship between the relative concentrations of the substrates in a reaction and the ambient temperature and the density of particles. We can derive this equation by using the partition function.

Given the dissociation reaction:

$$AB \overset{\Delta E}{\longleftrightarrow} A + B$$
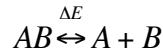
the partition function can be calculated as

$$Z = \sum_{k=0}^{N} \frac{(Z_{AB})^{N-k}}{(N-k)!} \frac{(Z_A)^k}{k!} \frac{(Z_B)^k}{k!}$$

where N is the number of AB molecules before dissociation has started. By searching for two successive terms that are closest to each other, we can find the most likely state of this system. This way we can avoid doing the sum, yet still extract information about the equilibrium concentrations of this reaction. Given N is large, we get:

$$\frac{Z_{AB}}{N-k} = \frac{Z_A}{k} \frac{Z_B}{k}$$

Now, it's a matter of writing down the individual partition functions for the particles involved. Z_A can be written as:

$$Z_A = V \left(\frac{2\pi M_A kT}{h^2} \right)^{3/2} Z_A(\text{int})$$

where the first term comes from the phase space of the coordinates of the particle and the second term is the internal partition function of that particle. Z_{AB} and Z_B can be written in

a similar fashion. Plugging this formula into the above one along with the other partition functions, after some more manipulation we get the Saha equation:

$$\frac{[n_A][n_B]}{[n_{AB}]} = \left(\frac{2\pi(M_A M_B / M_{AB})kT}{h^2}\right)^{3/2} \frac{Z_A(\text{int})Z_B(\text{int})}{Z_{AB}(\text{int})}$$

B. Dissociation and Ionization of Hydrogen

Now, the above formula can be used as a template for the reactions of interest for this write-up. The dissociation of molecular hydrogen and the ionization of atomic hydrogen:

$$H_2 \leftrightarrow 2H \leftrightarrow 2p^+ + 2e^-$$
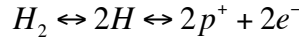
Letting the initial concentration of H_2 be n_0, we can write down the concentration of all particles of this reaction as:

$$[n_{H_2}] = (1-x)n_0$$
$$[n_H] = 2xn_0 - 2yn_0$$
$$[n_p] = 2yn_0$$
$$[n_e] = 2yn_0$$

Hence, the two Saha equations are:

$$\frac{(2(x-y)n_0)^2}{(1-x)n_0} = \left(\frac{2\pi(M_H/2)kT}{h^2}\right)^{3/2} \frac{(Z_H(\text{int}))^2}{Z_{H_2}(\text{int})}$$

$$\frac{(2yn_0)^2}{2(x-y)n_0} = \left(\frac{2\pi M_e kT}{h^2}\right)^{3/2} \frac{Z_p(\text{int})Z_e(\text{int})}{Z_H(\text{int})}$$

Plugging in the internal partition functions and taking the natural logarithm of both sides, we get:

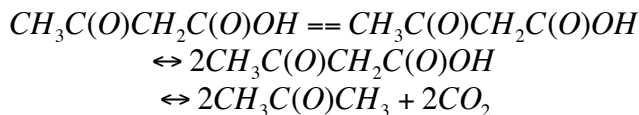$$Log\left[\frac{(2(x-y))^2}{(1-x)}\right] = \frac{E_2}{kT} - \frac{3}{2}Log\left[\frac{|E_2|}{kT}\right] + \frac{3}{2}Log\left[\frac{2\pi(M_H/2)|E_2|}{n_0^{2/3}h^2}\right]$$

$$Log\left[\frac{(2y)^2}{2(x-y)}\right] = \frac{E_1}{kT} - \frac{3}{2}Log\left[\frac{|E_1|}{kT}\right] + \frac{3}{2}Log\left[\frac{2\pi M_e |E_1|}{n_0^{2/3}h^2}\right]$$

where $E_1 = -13.6eV$ and $E_2 = -4.476eV$. Since the environment we're interested in is the surface of a star we will use $\sim10^{17}$ particles per cm^3 for the particle density n_0. We expect the dissociation rates to increase as the temperature increases. Hence, at extremely high temperatures we expect both x and y to be ~1, whereas at low temperatures both factors will be close to 0.

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C. Decarboxylation of Acetoacetic Acid

For the biological system that was chosen, we have the reaction:

$$CH_3C(O)CH_2C(O)OH == CH_3C(O)CH_2C(O)OH$$
$$\leftrightarrow 2CH_3C(O)CH_2C(O)OH$$
$$\leftrightarrow 2CH_3C(O)CH_3 + 2CO_2$$

where acetoacetic acid dimers connected by two hydrogen bonds with a bond strength of ~5kcal/mol (which translates to $6.948*10^{-13}$ ergs for two hydrogen bonds) breaks down to two acetoacetic acid molecules, which later on are carboxylated, meaning one CO_2 molecule is extracted from each acetoacetic acid.

Acetoacetic acid, a synthetically useful molecule, belongs to a group of chemicals named, β-keto acids (that belong to the larger group of carboxylic acids), which have the structure:

$$RC(O)CH_2C(O)OH$$

where the oxygen atoms in parentheses are have a double bond with the carbon atom coming before them. The product of this reaction, acetone, is used as an active ingredient in paint thinners and also is present in the human body in small amounts. Compared to carboxylic acids, β-keto acids decarboxylate easily due to the presence of a transition state that involves creating an enol, which later tautomerizes to a methyl ketone. This allows this specific reaction to have a relatively low temperature threshold.

The formulas we have derived for the previous reaction transfer nicely to this reaction. The new constants are given in the methods section below. As for the internal partition functions, we will limit our calculations to the dissociation energies of these reactions.

2. METHODS

Since the equations we have so far derived are nonlinear in nature, numerical methods were necessary to find the equilibrium concentrations of the substrates. The `FindRoot` function in *Mathematica* can be used to numerically solve a set of nonlinear equations. This algorithm uses Newton's method, which, given an initial guess, utilizes the Jacobian or a finite difference approximation to solve for the root of the step in process using a locally linear model.

Due to the wide range of temperatures, 0K to 40000K, `Do[ ]` was used to loop over the calculations of `FindRoot`. Given that the values we're looking for will be between 0 and 1, it was decided that choosing a precision goal of 5 significant figures was reasonable. This worked well for the temperature range that was chosen.

One of the problems that emerged in the programming phase was related to the initial guesses. If the initial guess is close to the actual root, then Newton's method can converge on a result very quickly. However, upon trial, it was seen that when the guess is not close to the actual root, *Mathematica* has a hard time pinning down reasonable results. Hence, a simple adjustment was made to improve on this problem by splitting the

loop into several different pieces with different initial x and y guesses chosen appropriately for each temperature interval. This greatly improved the solutions.

All constants were in c g s units:

$$k = 1.38 * 10^{-16} \, erg/K$$
$$h = 6.626 * 10^{-27} \, erg \cdot s$$
$$M_e = 9.109 * 10^{-28} \, g$$
$$M_H = 1.674 * 10^{-24} \, g$$
$$E_1 = -2.179 * 10^{-11} \, erg$$
$$E_2 = -7.171 * 10^{-12} \, erg$$
$$n_0 \sim 10^{17} \, cm^{-3}$$

Using the above constants we first plotted x and y values for a temperature range of 0K to 40000K. Then, by varying the particle density n_0 we observed the effects on the x and y values, again plotted in terms of the temperature.

Later, using the same method we looked at the decarboxylation of acetoacetic acid with the constants:

$$M_{AcetoaceticAcid} = 1.696 * 10^{-22} \, g$$
$$M_{Acetone} = 9.647 * 10^{-23} \, g$$
$$M_{CO_2} = 7.308 * 10^{-23} \, g$$
$$E_{HydrogenBonds} = -6.948 * 10^{-13} \, erg$$
$$E_{Decarboxylation} = -1.112 * 10^{-12} \, erg$$
$$n_0 = 6.022 * 10^{20} \, cm^{-3}$$

3. RESULTS

First, for the hydrogen reaction, the effects of temperature on the equilibrium positions of the reaction were investigated. We used $n_0 = 10^{17}$ cm^{-3} as our starting number density. In Figure 1, the x values have been plotted against the y values of the reaction in a parametric fashion. It can be seen that as x increases from 0 to 1 with an increase in temperature, there's barely any change in y. This means that atomic hydrogen does not become oxidized up to a relatively high temperature, which we can see also in Figure 2.

In Figure 2, we plot the x and y values against temperature. It can be seen that x has a steep increase between 2000K and 3000K, whereas y starts increasing around 8000K and keeps rising until about 30000K. This agrees with our expectations, since it requires more energy to ionize atomic hydrogen than to break molecular hydrogen into its components.
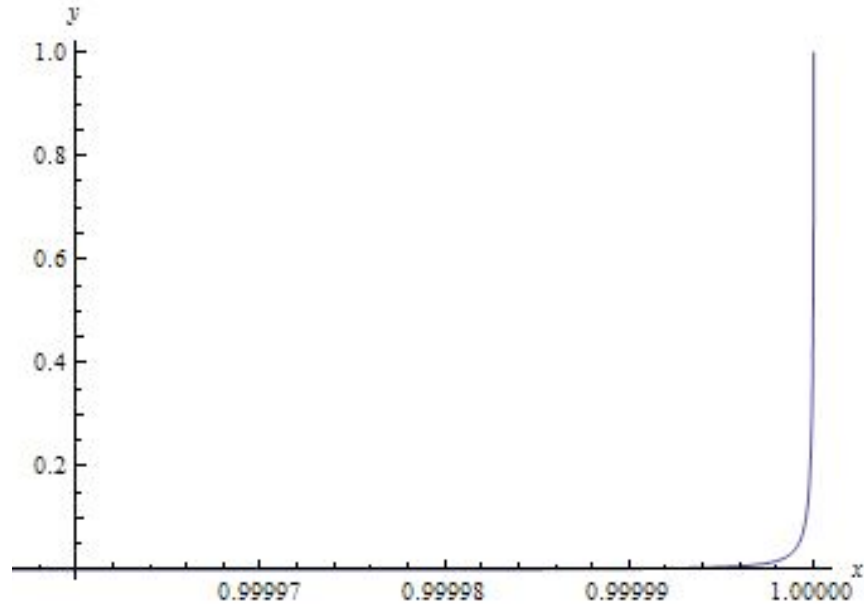
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Figure 1. Dissociation of hydrogen: A plot of x and y values for $n_0 = 10^{17}$ cm^{-3}. Each point represents a different temperature.
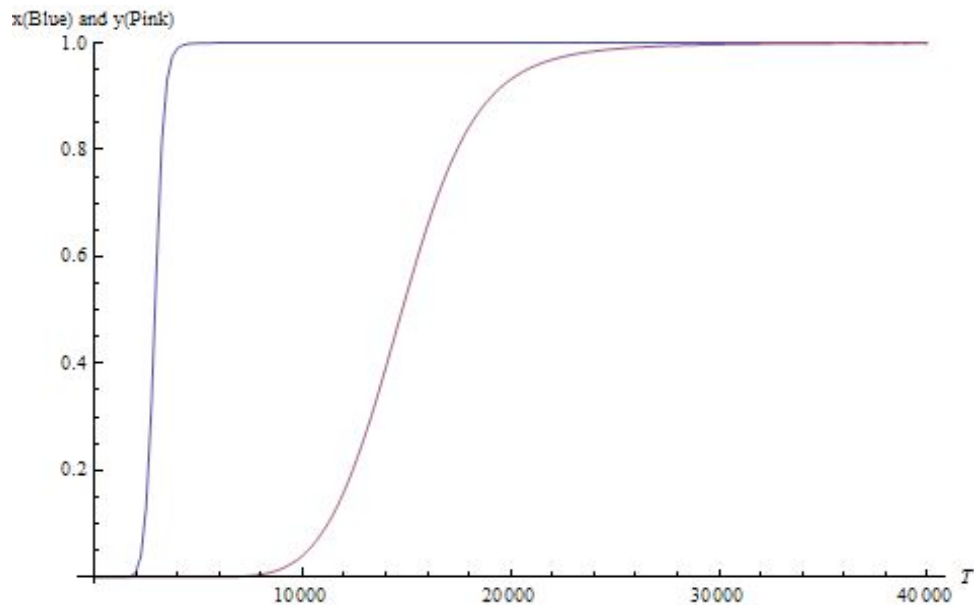

Figure 2. Values of x and y plotted against temperature. The blue curve is for x and the pink curve stands for y.

For purposes of exploring the effects of different particle density values, we repeated our method for the same reactions for different values of n_0. Above, in Figure 3, you see three graphs, respectively for $n_0 = 0.5*10^{17}$ cm^{-3}, $n_0 = 10^{18}$ cm^{-3} and $n_0 = 5*10^{18}$ cm^{-3}. It can be seen that as we increase the particle density, the equilibrium position shifts towards the left hand side of the reactions. In other words, for the y values to reach a value ~1, the temperature needs to be higher for higher densities. This is expected as increasing the

density of the gas means that we are increasing the pressure, forcing more collisions to take place. This pushes the equilibrium position to the left of the reaction.
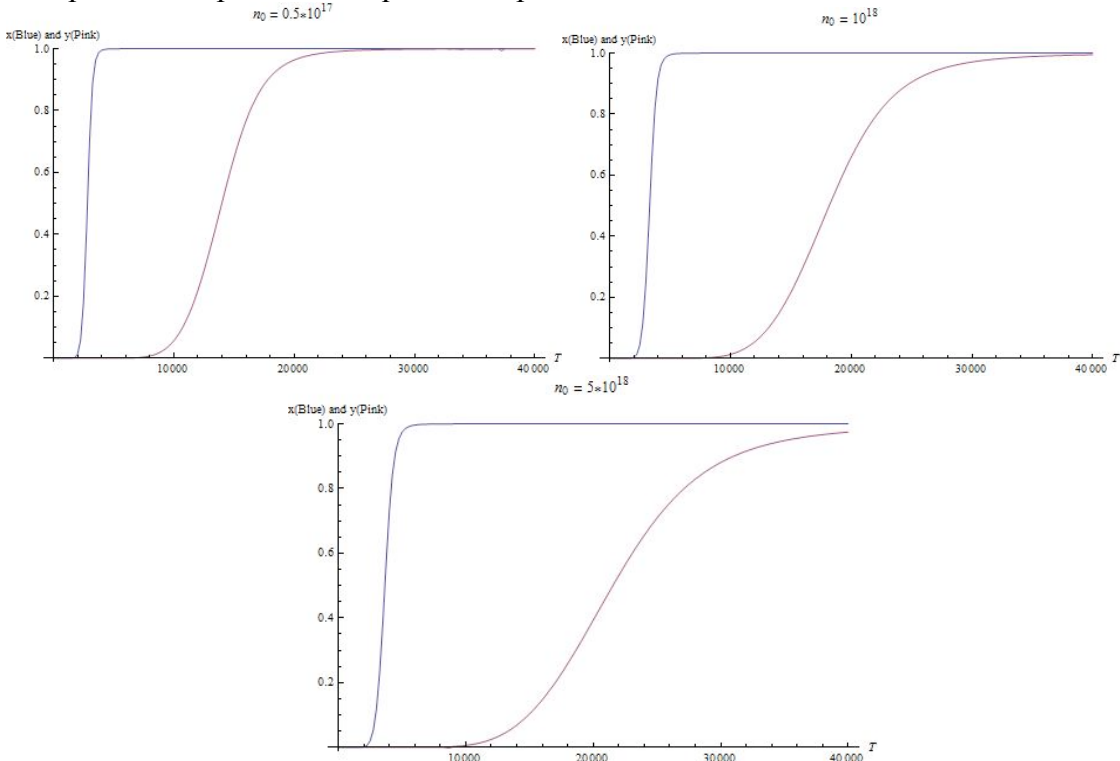

Figure 3. Reaction coordinates plotted against temperature for different particle densities; $n_0 = 0.5*10^{17}$ cm^{-3}, $n_0 = 10^{18}$ cm^{-3} and $n_0 = 5*10^{18}$ cm^{-3}.

For the decarboxylation of acetoacetic acid, our temperature range is much narrower. Again, we start at 0K and go up to ~1400K. We start seeing almost complete dissociation at ~1000K. At ~500K, practically all the hydrogen bonds are broken, hence we have no more dimers in the solution. Around ~1000K, almost all the acetoacetic acid molecules have been decarboxylated.

In this reaction, we are dealing with smaller energies and heavier molecules. Compared to the differences in energies between the dissociation of molecular and atomic hydrogen, we have smaller energy differences, hence the reaction coordinates are closer to each other in value at even low temperatures. We start observing an increase in y at around x = 0.6, which is quite different from the previous reaction.
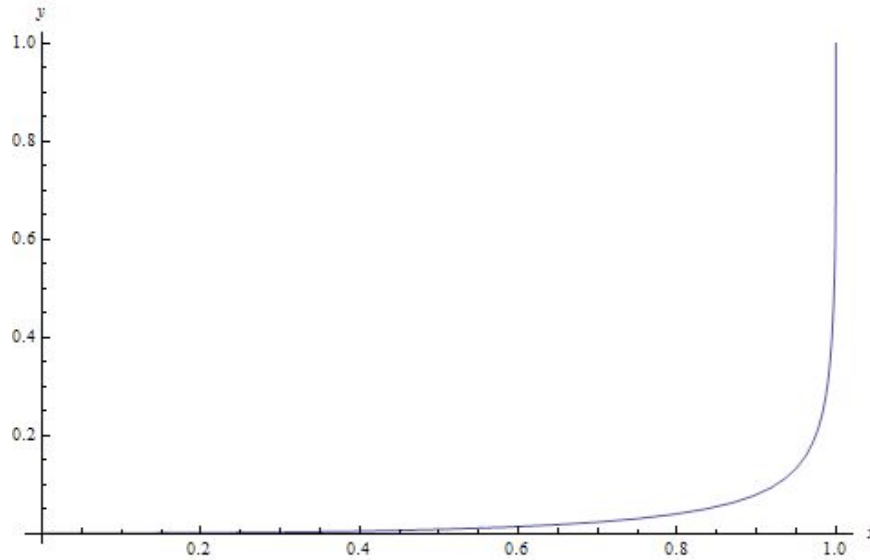
Figure 4. Decarboxylation: A plot of x and y values for $n_0 = 6.022 * 10^{20}$ cm^{-3}. Each point represents a different temperature.
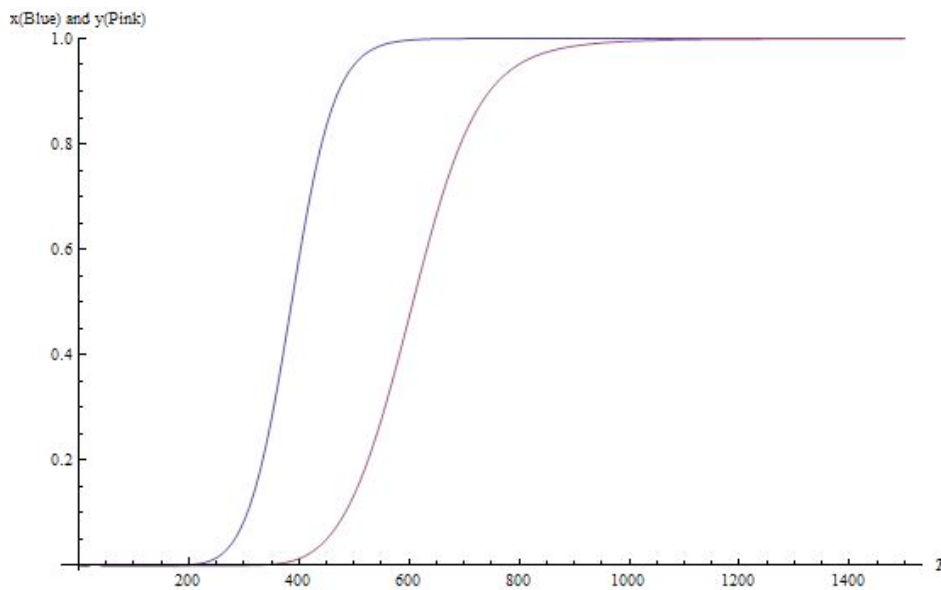

Figure 5. Values of x and y plotted against temperature. The blue curve is for x and the pink curve stands for y.

Saha's equation can be applied to a wide range of problems, from the compositional structure of stars to chemical reactions taking place in biological environments. The hardest part of this method is calculating the internal partition functions, however since we can truncate the sum in the partition function and limit it to the dissociation energies of the reactions, this method is still very handy at finding the equilibrium positions of the chemical reactions.

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5. REFERENCES

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