

8.6: Saha's Equation

Consider the reversible reaction



where A is a neutral atom and A^+ its first ion. Let N_0 , N_i , N_e be the numbers of neutral atoms, ions and electrons respectively, held in a box of volume V . Then

$$\frac{N_e N_i}{N_0} = S(T, P) \quad (8.6.2)$$

is the *Saha function*. It is a function of temperature and pressure, high temperature favouring ionization and high pressure favouring recombination. (Students of chemistry will recognize this as an application of Le Chatelier's principle.) The equation tells us the relative numbers of the three types of particle (i.e. the degree of ionization) in an equilibrium situation when the number of ionizations per second is equal to the number of recombinations per second.

Now the number of particles in a given energy level is proportional to the Boltzmann factor for that level, and the total number of particles is proportional to the sum of the Boltzmann factors for all the levels - i.e. to the partition function. Thus, using the symbol Q to denote partition functions, we have, for Saha's equation:

$$\frac{N_e N_i}{N_0} = \frac{Q_e Q_i}{Q_0}. \quad (8.6.3)$$

The partition function is the sum of the Boltzmann factors over all the states, translational and internal (electronic). The total energy of a particle is the sum of its translational and internal energies, so that total partition function is the product of its translational and internal partition functions, for which we shall use the symbol u . Therefore

$$\frac{N_e N_i}{N_0} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V \frac{u_e u_i}{u_0}. \quad (8.6.4)$$

Here $m = \frac{m_e m_i}{m_0}$, which is very little different from m_e .

The internal partition function of the electron is merely its statistical weight $2s + 1 = 2$. In calculating the internal partition functions of the atom and ion, it is, of course, essential to measure all energies from the same level - the ground level of the neutral atom, for example. You would not be so foolish, of course, as to calculate the partition function of the atom by using, in the Boltzmann sum, the energies of each level above the ground level of the atom, and then calculate the partition function of the ion by using the energies above some quite different level, such as the energy of the ground stage of the ion, would you? Most of us probably *would* be so foolish; we should, of course, add χ_i (the ionization energy) to each level of the ion. If we do calculate the partition function of the ion using energies above the ground level of the ion, we must then multiply the result, u_i , by $e^{-\chi_i/kT}$. Being even more careful, we should remember, from section 8.5, that the ionization energy is in practice lowered by a small amount $\Delta\chi_i$. Finally, let us now use the symbol n to denote number of particles per unit volume (so that $n = N/V$, and on no account to be confused with the quantum numbers n used in section 8.5) and we arrive at the usual form for Saha's equation:

$$\frac{n_e n_i}{n_0} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \frac{2u_i}{u_0} \exp\left(-\frac{(\chi_i - \Delta\chi_i)}{kT}\right). \quad (8.6.5)$$

It might be noted that $\Delta\chi_i$ is a function of n_e , which leads to a slight complication in the computation of Saha's equation, which we shall encounter in one of the problems that follow.

It should be remarked that Saha's equation played an extremely important role in the understanding of the stellar spectral sequence. As is well known, the sequence of spectral types OBAFG... is a result of the degree of ionization and excitation of the elements as a function of temperature, and the difference in the degree of ionization between main sequence stars and giants of a given temperature is the result of the higher degree of ionization in the relatively low pressure atmospheres of the giant stars. This could not be understood at a quantitative level until the development of Saha's equation and its application to stellar atmospheres by Saha, Fowler, Milne and Payne (later Payne-Gaposhkin) in the 1920s.

Problems.

Problem 1. Verify that equation 8.6.5 balances dimensionally.

Problem 2. In the bad old days, we did calculations using logarithm tables! You probably will never have to do that, but this exercise will nevertheless turn out to be useful. Show that Saha's equation can be written as

$$\log \frac{n_e n_i}{n_0} = A + \frac{3}{2} \log T + \log \frac{u_i}{u_0} - B \left(\frac{V_i - \Delta V_i}{T} \right) \quad (8.6.6)$$

and determine the numerical value of the constants A and B if n is expressed in m^{-3} , T is in K , V_i is the ionization potential in volts, and logarithms are common logarithms (i.e. to the base 10). I make them $A = 21.68$ and $B = 5039.7$. It is common also to write equation 8.6.6 in the form

$$\log \frac{n_e n_i}{n_0} = 27.24 - \frac{3}{2} \log \theta + \log \frac{u_i}{u_0} - \theta (V_i - \Delta V_i), \quad (8.6.7)$$

in which $\theta = 5039.7/T$.

Problem 3. You are going to calculate the Saha function for hydrogen, and so you need the partition functions for the electron, the neutral hydrogen atom and the hydrogen ion. The electron is easy. Its spin is $1/2$, so its partition function is 2, as already discussed and indeed already incorporated into Saha's equation. The partition function for neutral hydrogen can be taken to be the statistical weight of its $n = 1$ shell, which is $2n^2 = 2$. Now what about the statistical weight of the hydrogen ion? The hydrogen ion is a proton, which has spin $= 1/2$. Therefore, as for the electron, should the partition function be 2? The answer is no! When calculating the Saha equation for hydrogen, you should take the partition function of the proton to be 1. This probably seems entirely illogical and you are probably quite sure that I am wrong. But before coming to this conclusion, read again the last paragraph of section 8.4 and the first paragraph of section 8.5i. You can include the effect of the proton spin provided that you take it into account for both H and H^+ . If you insist that the statistical weight of the proton is 2, you must also insist that the statistical weight of the $n = 1$ shell of H is $4n^2 = 4$. As with the Boltzmann equation, you usually need not be concerned with nuclear spin - it cancels out in u_i/u_0 . There is nothing, however, to cancel out the factor 2 for the electron partition function.

Problem 4. A kilogram of water is contained in a box of volume one cubic metre. The box is made of material that won't melt or vaporize. (!) Draw a graph showing, as a function of temperature, from 10,000 K to 20,000 K, the logarithm of the numbers per unit volume of each of the species e , H, H^+ , O, O^+ . (Assume there are no higher ionization stages, and no molecules.)

This is going to be difficult, and will involve some computation. The first thing you are going to need to do is to calculate the Saha functions of the species involved as a function of temperature, and for this, you will need the partition functions. For the electron, the partition function is 2 and is already incorporated in the Saha equation. As discussed in Problem 3, the partition function of H^+ should be taken to be 1, and, as for the electron, it is mercifully independent of temperature. For neutral H, the statistical weight of the ground shell is 2, and, as you will already have discovered if you carried out the little calculation in section 8.5ii, you can probably take this to be the partition function at all temperatures between 10,000 and 20,000 K. The ground term of neutral oxygen is ^3P , and the first excited term is ^1D at a term value of 15868 cm^{-1} . Probably only the ground term contributes appreciably to the partition function, but you might want to check that. The ground term of O II is $^4\text{S}^o$ and the first excited term is a long way up. Thus, for all species, you can probably take the partition function to be the statistical weight of the ground term and independent of temperature. You are very lucky that I did not throw a metal into the mix!

The ionization limits of H and O are at 101678 and 109837 cm^{-1} respectively. We don't yet know by how much, $\Delta\chi_i$ the ionization energy is lowered, so we'll ignore $\Delta\chi_i$ to begin with. You now have enough information to calculate the Saha functions for hydrogen and for oxygen as a function of temperature.

We have been asked to calculate the numbers of five species and we are therefore going to need four equations. We started with one kilogram of water. We know that 18 grams of water contain A molecules, where A is Avogadro's number. (You may want to look up the exact molar mass of H_2O .) Thus, we started with $1000A/18$ molecules. Let's call that number N .

Now see if you agree with the following five equations.

$$N_{\text{H}} + N_{\text{H}^+} = 2N \quad (8.6.8)$$

$$N_{\text{O}} + N_{\text{O}^+} = N \quad (8.6.9)$$

$$N_{\text{H}^+} + N_{\text{O}^+} = N_e \quad (8.6.10)$$

$$N_e N_{\text{H}^+} = V S_{\text{H}} N_{\text{H}} \quad (8.6.11)$$

$$N_e N_{\text{O}^+} = V S_{\text{O}} N_{\text{O}} \quad (8.6.12)$$

We do indeed have five equations in the five unknowns, and all other quantities in the equations are known. The first two express the stoichiometry of the water molecule. The third expresses electrical neutrality. The last two are Saha's equations for hydrogen and oxygen. They five equations are not very difficult equations, although the last two are nonlinear, which makes them slightly awkward. We can make them a little easier. I am going to re-write them:

$$N_H + N_{H^+} - 2N = 0 \quad (8.6.13)$$

$$N_O + N_{O^+} - N = 0 \quad (8.6.14)$$

$$N_{H^+} + N_{O^+} - N_e = 0 \quad (8.6.15)$$

$$VS_H N_H - N_e N_{H^+} = 0 \quad (8.6.16)$$

$$VS_O N_O - N_e N_{O^+} = 0 \quad (8.6.17)$$

If we now, just for the moment, suppose that N_e is a quantity whose value is known. In that case, equations 8.6.13 to 8.6.17 would comprise five *linear* equations in just *four* unknowns. The condition for these equations to be consistent is that the determinant of the coefficients and the constant terms be zero:

$$\begin{vmatrix} 1 & 1 & 0 & 0 & -2N \\ 0 & 0 & 1 & 1 & -N \\ 0 & 1 & 0 & 1 & -N_e \\ VS_H & -N_e & 0 & 0 & 0 \\ 0 & 0 & VS_O & -N_e & 0 \end{vmatrix} = 0 \quad (8.6.18)$$

If I have done my algebra right (you might like to check this), this is a cubic equation in N_e :

$$N_e^3 + V(S_O + S_H)N_e^2 + V[VS_H S_O - (2S_H + S_O)N]N_e - 3V^2 S_H S_O N = 0. \quad (8.6.19)$$

You can now solve this for N_e . Remember, however, that, in calculating the Saha functions, you ignored the lowering of the ionization potential ΔV_i , so what you have found is but a first approximation for N_e . This is a function of the electron density. One rather old formula, due to Unsöld, is

$$\Delta V_i = 7 \times 10^{-5} n_e^{1/3}, \quad (8.6.20)$$

where V_i is in volts and $n_e (= N_e/V)$ is in m^{-3} (indicating that the lowering of the potential is proportional to the distance between the charged particles.). If you can find a more recent and perhaps better formula, by all means use it. You can use your first approximation for n_e to calculate the Saha functions, and then repeat the entire calculation and continue to iterate until you obtain an acceptably small change in n_e . It is probable that only one iteration will be necessary. Having found n_e (and N_e) it is then straightforward to find the remaining unknowns from equation 8.6.13 to 8.6.17. Just make sure that you make use of all five equations as a check for arithmetic mistakes.

Problem 5. A bottle of methyl cyanate CH_3CNO is held in a cylinder with a movable piston such that the pressure remains constant at one pascal. Heat it up to some temperature at which you can assume that the only species present are electrons and the neutral atoms and singly ionized stages of C, H, O and N - i.e. no higher ionization stages and no molecules. The cylinder and piston are not allowed to melt - they are required only to provide constant pressure conditions, in contrast to the previous problem in which you had a constant volume. You have nine unknowns, and you will need nine equations. In this problem you are asked merely to write down the nine required equations, not necessarily to solve them unless you particularly want to. There will be Saha equations for each element, an equation expressing electrical neutrality, and four equations reflecting the stoichiometry. You may assume the ideal gas equation $P = nkT$.

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