

Saha Ionisation Equation

Ionisation energies of atoms are of the order of tens of eV (for hydrogen, it is $13.6 eV$). The equivalent temperature is $\sim 10^4 - 10^5$ K. Such high temperatures are easily realised in various astrophysical situations (stars, in particular). Hence, it is of importance to astrophysical studies. Thermodynamically, ionisation can be looked upon as a chemical reaction where one reactant transforms into two new ones (or vice-versa). Such a treatment was first developed by Meghnad Saha, and the essence is captured in the famous *Saha Ionisation equation*.

In general, a process that can change the number of particles of a certain kind, is called a chemical reaction. A generic reaction is written as,

$$\sum_j R_j \alpha_j = 0, \quad (105)$$

where, R_j and α_j are the chemical symbol and the no. of particles of species j taking part in the reaction. Since, reactions take place in equilibrium with their surroundings, temperature and pressure remain constant, same as that of the surroundings. The appropriate thermodynamics potential for the overall system is then the Gibb's potential with the equilibrium condition given by,

$$dG = -S dT + V dP = 0. \quad (106)$$

(It is, of course, conceivable to have reactions taking place under different circumstances. An appropriate thermodynamic potential need to be used to describe such reactions.) Now, for each particle species we have,

$$dG_j = \mu_j dN_j, \quad \text{with } dT, dP = 0, \quad (107)$$

which, in equilibrium, implies,

$$dG = \sum_j dG_j = \sum_j \mu_j dN_j = 0. \quad (108)$$

However, the number of particles, of a particular species, would change strictly according to the specific reaction being considered. Each time the reaction happens, the number of each reactant R_j changes only by n_j . Thus, the total change, dN_j must be proportional to α_j . At equilibrium then, the chemical potentials of different reactants satisfy the relation

$$\sum_j \mu_j \alpha_j = 0, \quad (109)$$

which is the law of chemical equilibrium. It should be remembered that we need to use the total chemical potential (inclusive of the rest mass of the particle) here. Because, this condition implies that

$$\sum_j \mu_j^{NR} \alpha_j = 0, \quad (110)$$

only if $\sum_j m_j \alpha_j = 0$, i.e., the total rest mass is invariant through the reaction in consideration ($\mu^{NR} = \mu - mc^2$). Since, that is not true of all reactions (notably, the fusion reactions in stars) it is not appropriate to use μ^{NR} in general.

Let us now suppose that the reactants can be treated as classical ideal gases. The single particle partition function for an ideal gas is given by,

$$Q_1 = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \frac{V}{\Lambda_T}, \quad (111)$$

where Λ_T can be thought of as the thermal de Broglie volume associated with a particle. Then the partition function for an N -particle ideal gas is,

$$Q = \frac{1}{N!} \left(\frac{V}{\Lambda_T} \right)^N, \quad (112)$$

and the grand partition function is

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{Q^N}{N!}. \quad (113)$$

Now,

$$\begin{aligned} P &= k_B T \left. \frac{\partial \ln \mathcal{Z}}{\partial V} \right|_{T,\mu} \\ &= \frac{e^{\beta\mu}}{\beta \Lambda_T}. \end{aligned} \quad (114)$$

Using the ideal gas equation of state $PV = Nk_B T = N/\beta$ we find

$$n = \frac{N}{V} = \frac{e^{\beta\mu}}{\Lambda_T}. \quad (115)$$

If the particles of the reactants (assumed to behave like classical, ideal gases) have internal degrees of freedom, this formula is modified to

$$n = \frac{q e^{\beta\mu}}{\Lambda_T}, \quad (116)$$

where q is the contribution to the partition function due to the internal degrees of freedom, implying

$$\mu = \frac{1}{\beta} \ln \left(\frac{n \Lambda_T}{q} \right). \quad (117)$$

Using this in the equation for chemical equilibrium we have,

$$\sum_j \alpha_j \ln \left(\frac{n_j \Lambda_j}{q_j} \right) = 0, \quad \Rightarrow \quad \prod_j n_j^{\alpha_j} = \prod_j \left(\frac{q_j}{\Lambda_j} \right)^{\alpha_j}. \quad (118)$$

Here Λ_j is the quantum volume for the j -th species. The contribution of the internal degrees of freedom to the partition function can be written as

$$q = q^0 e^{-\beta\epsilon^0}, \quad (119)$$

where ϵ^0 is the energy of the ground state of the internal degrees of freedom and q^0 is the internal partition function for zero ground state energy. If there are only one kind of particles, then one

can set $\epsilon^0 = 0$, but it can not be done when different species of particles are involved and we have

$$\Pi_j n_j^{\alpha_j} = \Pi_j \left(\frac{q_j^0 e^{-\beta \epsilon_j^0}}{\Lambda_j} \right)^{\alpha_j}. \quad (120)$$

For example, consider



where X and Y denote two kinds of particles and XY denote their bound state. Then in equilibrium, the number densities of X , Y and XY are governed by,

$$\frac{n_X n_Y}{n_{XY}} = \frac{q_X^0 q_Y^0}{q_{XY}^0} \frac{\Lambda_{XY}}{\Lambda_X \Lambda_Y} \exp \left[\beta (\epsilon_{XY}^0 - \epsilon_X^0 - \epsilon_Y^0) \right]. \quad (122)$$

The quantity multiplying β in the exponent is the binding energy of the molecule XY if the atoms X and Y react to form it.

Ionisation : Consider an ionisation equation of the following form



where X can be looked upon as the bound state of the ion X^+ and the electron. As the masses of the ion and the atom are almost equal we have $\Lambda_{X^+} \simeq \Lambda_X$. Therefore,

$$\frac{n_{X^+} n_{e^-}}{n_X} = \frac{q_{X^+}^0 q_{e^-}^0}{q_X^0} \frac{e^{-\beta \epsilon}}{\Lambda_e}. \quad (124)$$

The first factor on the right hand side usually contains the degeneracy factors due to spin etc. If we define the fraction of the particles in the following manner,

$$n_X + n_{X^+} = n_t, \quad f = \frac{n_{X^+}}{n_t}, \quad (125)$$

then, with charge neutrality ($n_{X^+} = n_e$)

$$\frac{f^2}{1-f} = \frac{q_{X^+}^0 q_{e^-}^0}{q_X^0} \frac{e^{-\beta \epsilon}}{n_t \Lambda_e}. \quad (126)$$

This is the **Saha Ionisation Equation**. In the NR limit $\Lambda \propto T^{-3/2}$, so at high temperatures, the right hand side becomes very large. This means at high temperatures the ionisation fraction is very large. As $T \rightarrow 0$, we have $f \rightarrow 0$ although the validity of this equation should be suspect in this limit because the gases may not behave as classical ideal gases.