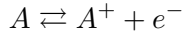


E4213: Chemical equilibrium $A \rightleftharpoons A^+ + e^-$

Submitted by: Yaron de Leeuw

The problem:

N atoms of type A were put into a box of volume V . The system has reached a state of thermochemical equilibrium



The solution should be expressed by the masses m_e, m_A , the ionization energy ε , the temperature T and the gas density $n = \frac{N}{V}$.

- (1) Find the percent of ionized atoms, if the electrons and A atoms form a classical (Boltzmann) gas. ($T \gg T_1$).
- (2) Find the percent of ionized atoms, if the electrons form a low temperature Fermi gas, while the A atoms continue to form a classical gas. ($T_1 \gg T \gg T_0$).
- (3) Define T_0 and T_1 .

The solution:

The free energy of the system after N_i atoms have been ionized is:

$$F = F_A(N - N_i) + F_{A^+}(N_i) + F_{e^-}(N_i)$$

So the probability for N_i ionized atoms should behave like:

$$p(N_i) \propto e^{-\beta F}$$

The most probable value for N_i will be the minimum of the free energy:

$$\begin{aligned} \frac{dF}{dN_i} &= 0 \\ -\mu_A + \mu_{A^+} + \mu_{e^-} &= 0 \end{aligned}$$

(1) The electrons form a classical Boltzmann gas. Because the spin of the A atoms is unknown, we choose to consider the atoms and the electrons to be "spinless". The generalization of the degeneracy for particles with non zero spin is trivial. The single particle partition function for an atom A is:

$$Z_A = \frac{V}{\lambda_{TA}^3}$$

Where λ_{TA} is defined by

$$\lambda_{TA} = \sqrt{\frac{2\pi}{m_A T}}$$

For the ionized A^+ atoms, the partition function will be:

$$Z_{A^+} = \frac{V}{\lambda_{TA^+}^3} e^{-\beta\varepsilon}$$

The multiparticle partition function for N atoms of type A is:

$$Z_{AN} = \frac{Z_A^N}{N!}$$

So the chemical potential μ is:

$$\mu_A = -\frac{d}{dN} T \ln Z_{AN} = T \ln \frac{N}{Z_A}$$

The same calculation will yield similar results for A^+ and e^- . Putting these results into the chemical equilibrium equation, we obtain:

$$\begin{aligned} -T \ln \frac{N - N_i}{Z_A} + T \ln \frac{N_i}{Z_{A^+}} + T \ln \frac{N_i}{Z_{e^-}} &= 0 \\ \frac{N - N_i}{N_i^2} &= \frac{Z_A}{Z_{A^+} Z_{e^-}} \\ \frac{N_i^2}{N^2} + \frac{1}{N} \frac{Z_{A^+} Z_{e^-}}{Z_A} \frac{N_i}{N} - \frac{1}{N} \frac{Z_{A^+} Z_{e^-}}{Z_A} &= 0 \\ \frac{N_i}{N} &= \frac{1}{2N} \frac{Z_{A^+} Z_{e^-}}{Z_A} \left(-1 \pm \sqrt{1 + \frac{4N Z_A}{Z_{A^+} Z_{e^-}}} \right) \\ \frac{N_i}{N} &= \frac{1}{2N} \left(\frac{T m_e (m_e + m_A)}{2\pi m_A} \right)^{\frac{3}{2}} e^{-\beta \varepsilon} \left(-1 + \sqrt{1 + \frac{4N}{V} \left(\frac{2\pi m_A}{T m_e (m_e + m_A)} \right)^{\frac{3}{2}} e^{\beta \varepsilon}} \right) \end{aligned}$$

In the last step we have chosen the positive solution, as the number of ionized atoms cannot be less than 0.

(2) For a Fermi gas we have the following expression:

$$\frac{N}{V} = \frac{1}{\lambda_T^3} F_{3/2}(e^{\beta \mu})$$

Putting in the chemical potential equation we obtain:

$$\begin{aligned} \frac{N_i}{V} &= \frac{1}{\lambda_{T_e}^3} F_{3/2}(e^{\beta(\mu_A - \mu_{A^+})}) = \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{\frac{N - N_i}{Z_A}}{\frac{N_i}{Z_{A^+}}} \right) = \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} \frac{Z_{A^+}}{Z_A} \right) \\ &= \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} \left(\frac{m_{A^+}}{m_A} \right)^{\frac{3}{2}} e^{-\beta \varepsilon} \right) \approx \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} e^{-\beta \varepsilon} \right) \end{aligned}$$

The first order approximation of $F_{3/2}$ gives exactly the same solution as before.

(3) The necessary condition for Boltzmann's approximation is $n \lambda_T^3 \ll 1$.

Putting in λ_T , this gives

$$n \left(\frac{2\pi}{mT} \right)^{\frac{3}{2}} \ll 1 \quad \Rightarrow \quad n \left(\frac{2\pi}{m} \right)^{\frac{3}{2}} \ll T^{\frac{3}{2}} \quad \Rightarrow \quad T \gg n^{\frac{2}{3}} \frac{2\pi}{m}$$

For the electrons, this temperature will be:

$$T_1 = n^{\frac{2}{3}} \frac{2\pi}{m_e}$$

And for the A atoms this will be:

$$T_0 = n^{\frac{2}{3}} \frac{2\pi}{m_A}$$

Because the mass of the atoms is much larger than the mass of the electrons, $T_1 \gg T_0$, there exists a wide range of temperatures which satisfy the conditions for section (2).