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

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 thermo-chemical equilibrium

$$A \rightleftarrows A^+ + e^-$$

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:

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

(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:

$$-T \ln \frac{N - N_i}{Z_A} + T \ln \frac{N_i}{Z_{A^+}} + T \ln \frac{N_i}{Z_{e^-}} = 0$$

$$\frac{N - N_i}{N_i^2} = \frac{Z_A}{Z_{A^+} Z_{e^-}}$$

$$\frac{N_i^2}{N^2} + \frac{1}{N} \frac{Z_{A^+} Z_{e^-}}{Z_A} \frac{N_i}{N} - \frac{1}{N} \frac{Z_{A^+} Z_{e^-}}{Z_A} = 0$$

$$\frac{N_i}{N} = \frac{1}{2N} \frac{Z_{A^+} Z_{e^-}}{Z_A} \left(-1 \pm \sqrt{1 + \frac{4N Z_A}{Z_{A^+} Z_{e^-}}} \right)$$

$$\frac{N_i}{N} = \frac{1}{2} \frac{V}{N} \left(\frac{T m_e (m_e + m_A)}{2\pi m_A} \right)^{\frac{3}{2}} e^{-\beta\varepsilon} \left(-1 + \sqrt{1 + \frac{4N}{V} \left(\frac{2\pi m_A}{T m_e (m_e + m_A)} \right)^{\frac{3}{2}} e^{\beta\varepsilon}} \right)$$

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:

$$\frac{N_i}{V} = \frac{1}{\lambda_{T_e}^3} F_{3/2}(e^{\beta(\mu_A - \mu_A^+)}) = \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{\frac{N-N_i}{Z_A}}{\frac{N_i}{Z_{A^+}}} \right) = \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} \frac{Z_{A^+}}{Z_A} \right)$$

$$= \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} \left(\frac{m_{A^+}}{m_A} \right)^{\frac{3}{2}} e^{-\beta\varepsilon} \right) \approx \frac{1}{\lambda_{T_e}^3} F_{3/2} \left(\frac{N - N_i}{N_i} e^{-\beta\varepsilon} \right)$$

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).