## DETERMINATION OF THE COMPOSITION OF A TWO-TEMPERATURE PLASMA

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1. In plasmas the variation of the characteristic parameters of the system sometimes proceeds much more slowly than the ionization and recombination processes. In this case the plasma composition is determined not by the differential equations of chemical kinetics, but by finite relations. Thus, in a one-temperature plasma, the Saha equation, which is valid for total thermodynamic equilibrium is used to determine the concentrations of the components.

Due to the difference in the mechanisms of energy supply to electrons and heavy particles (atoms and ions), a marked difference in the temperatures of the translational degrees of freedom of the heavy and light plasma components is possible. This is also partly attributable to the fact that the rate of equalization of these temperatures is proportional to the ratio of the electron mass m to the heavy particle mass M, i.e., is a very small quantity. Naturally, for a two-temperature plasma the Saha equation cannot be used in its usual form, but requires modification. Such a modification was described in [1, 2] for the case when energy is supplied mainly to the electron gas and, consequently, the electron temperature exceeds the heavy particle temperature. There it was proposed to use the Saha equation with the over-all plasma temperature replaced by the electron temperature; this was justified on the basis of qualitative considerations consisting in that electrons, having a greater velocity than atoms and ions, play the main role in ionization and recombination processes. Data obtained in this way have been confirmed experimentally [1, 3]. At present, the Saha equation with the electron temperature is widely used for investigating two-temperature plasma. Nevertheless, it is of interest to derive the equation on the basis of the thermodynamic approach, applicable to one-temperature plasma, using physically justifiable additional assumptions. This problem is the subject of the present article. Note that such a derivation is also interesting because it makes it possible to estimate more accurately the limits of applicability of the equation from the conditions that ensure satisfaction of the assumptions.

2. Consider a quasineutral plasma consisting of electrons, neutrals and ions. Let  $N_j$  be the number of ions ionized j times; in particular,  $N_0$  is the number of neutral atoms. In view of the quasineutrality, the number of electrons is

$$N_e = 1N_1 + 2N_2 + \ldots + j_{\max}N_{j\max},$$

where the summation is taken over ions of all multiplicities 0, 1,...,  $j_{max}$ .

We assume that the plasma may be divided into a finite number of subsystems, within each of which thermodynamic equilibrium exists. Such an assumption is the basis of any phenomenological approach and is confirmed both theoretically and experimentally by the fact that equilibrium is usually established more rapidly within each subsystem than in the system as a whole. We take the following three systems as the equilibrium subsystems: the sybsystem formed by the translational degrees of freedom of electrons; the subsystem formed by the translattional degrees of freedom of heavy particles; and the subsystem formed by the electron levels of these particles. Let  $T_e$ , T, and  $T_i$  be the temperatures of the corresponding subsystems.

We will consider the subsystem interaction mechanism, limiting ourselves to cases where the role of radiation in the mechanisms of energy exchange and change of composition is not significant and the electron concentration is not too low. In the cases under investigation, energy exchange between translational degrees of freedom of electrons and heavy particles takes place much more slowly than do ionization and recombination because of the smallness of the ratio m/M. For the same reason, and in view of the fact that  $T_e \geq T$ , inelastic collosions of heavy particles with electrons play a much greater role than do inelastic collisions with heavy particles accompanied by a change in their total kinetic energy. This makes it possible to ignore excitation of electron levels and ionization caused by heavy particle collisions and to consider only collisions with electrons in these processes. Moreover, in considering cases where ionization and recombination are much more rapid than the variation of the characteristic parameters of the problem, it is natural to assume that energy exchange between the electron gas and the electron levels of atoms and ions also takes place quite rapidly. Hence,  $T_i \approx T_e$ , which is equivalent to combining two subsystems into one.

With the given assumptions, the basic recombination mechanism is the triple collision mechanism, where, due to the larger electronion collision cross sections (in comparison with ion-ion and ion-atom collisions) and the high electron velocity, the main role is played by collisions with the third particle-the electron. For recombination, as for ionization, we can ignore the energy acquired or given up in these processes by the translational degrees of freedom of atoms and ions. Thus, when the given constraints and assumptions are satisfied, the plasma may be considered as consisting of two subsystems: the subsystem formed by the translational degrees of freedom of atoms and ions and the subsystem formed by their electron levels and the electron gas. Within these subsystems there is thermodynamic equilibrium with temperatures T and Te, respectively. Changes in composition occur at the expense of the energy of the second system. Energy exchange between subsystems takes place much more slowly than does ionization and recombination.

3. On the basis of the above assumptions we obtain the expression  $\ensuremath{\mathsf{N}}$ 

$$E = \frac{3}{2} NkT + \frac{3}{2} N_e kT_e + \sum_{j=0}^{j_{\max}} N_j \left[ E_j(T_e) + \sum_{l=0}^{j} \chi_l \right]$$

$$\left( N = \sum_{j=0}^{j_{\max}} N_j, N_e = \sum_{i=0}^{j_{\max}} iN_j \right)$$

$$S = \frac{5}{2} kN + kN \ln \left[ V \left( \frac{2\pi M k}{h^2} \right)^{3/e} T^{\gamma_e} \right] + \frac{5}{2} kN_e - kN_e \ln N_e + \frac{1}{2} kN_e \ln \left[ 2V \left( \frac{2\pi m k}{h^2} \right)^{3/e} T_e^{3/e} \right] + \frac{5}{2} \sum_{i=0}^{j_{\max}} N_j \left[ k \ln u_j (T_e) + \frac{E_j (T_e)}{T_e} - k \ln N_j \right]$$

for the internal energy E and entropy S of a plasma occupying a volume V, assuming that the plasma as a whole and each of its components form an ideal gas and using the general principles of statistical physics and thermodynamics.

Here k and h are the Boltzmann and Planck constants; N is the total number of heavy particles:  $\chi_j$ ,  $E_j$ , and  $u_j$  are, respectively, the ionization energy, electron level energy, and the statistical sum of the electron levels of an ion ionized j times. In this case  $\chi_0 = 0$  and  $E_j = kT_e^2 d [\ln u_j (T_e)]/dT_e$ .

Let us consider the changes in entropy which may occur with a change in the composition of a quasi-neutral plasma containing a constant number of heavy particles and confined in an adiabatically insulated vessel of constant volume V. i.e., let us find an expression for the possible variation of entropy S in terms of the variation of concentrations and temperatures for  $\delta V = \delta N = \delta E = 0$ . These last conditions impose definite constraints on the variations  $\delta N_0, \ldots, \delta N_{j_{\text{Imax}}}$ ,  $\delta T_e$  and  $\delta T$ . To account for these constraints we use the method of Lagrange multipliers which, of course, leads to the same results as the direct elimination of the dependent variations. We construct the function  $\Omega = S + \lambda E + \mu N$ , where  $\lambda$  and  $\mu$  are constant factors. For all deviations from the given state that do not affect E and N, the variations of  $\Omega$  and S coincide. Therefore, taking account of the expressions for S, E, N, and N<sub>e</sub>, we find

$$\begin{split} \delta S &= \delta \Omega = \sum_{j=0}^{j_{\text{max}}} k \left\{ i \left[ \frac{3}{2} (1 + \lambda T_e) + \ln \left[ 2V \left( \frac{2\pi mk}{h^2} \right)^{3/2} T_e^{3/2} \right] - \right. \\ &- \ln N_e \right] - 1 - \ln N_j + \ln u_j (T_e) + \frac{E_i (T_e)}{k} \left( \lambda + \frac{1}{T_e} \right) + \right. \\ &+ \frac{\lambda}{k} \sum_{l=0}^{j} \chi_l + \mu \right\} \delta N_j + \left( \lambda + \frac{1}{T_e} \right) \left[ \frac{3kN_e}{2} + \sum_{j=0}^{j_{\text{max}}} N_j \frac{dE_j (T_e)}{dT_e} \right] \delta T_e + \\ &+ \frac{3 kN}{2} \left( \lambda + \frac{1}{T} \right) \delta T \,. \end{split}$$

Choosing  $\lambda$  and  $\mu$  so that the coefficients of  $\delta N_0$  and  $\delta T$  vanish, we obtain

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$$\delta S = \delta \Omega = \sum_{j=1}^{J_{\max}} k \left\{ j \left( \ln \left[ 2V \left( \frac{2\pi m k}{h^2} \right)^{3/2} T_e^{3/2} \right] - \ln N_e 
ight) - \ln rac{N_j}{N_0} + \ln rac{u_j (T_e)}{u_0 (T_e)} - rac{1}{kT_e} \sum_{l=0}^j \chi_l \right\} \delta N_j + rac{3}{2} k N \left( rac{1}{T} - rac{1}{T_e} 
ight) \delta T.$$

In view of our assumptions on the mechanism of energy exchange in ionization and recombination, variations of T associated with change in composition should be neglected. The variations  $\delta N_j$  left in the expression for  $\delta S$  are independent and in the equilibrium state with respect to composition may assume both positive and negative values. Since the entropy of a closed, adiabatically insulated system in a constant-volume vessel, cannot decrease, in this state the coefficients of  $\delta N_1,\ldots,\delta N_{j_{\rm IIII}}$  must vanish. Hence, after introducing the concentrations  $n_j = N_j/V$  and  $n_e = N_e/V$  and making certain transformations, we get the  $j_{\rm IIII}$ 

$$\frac{n_{j}n_{e}}{n_{j-1}} = \frac{2u_{j}(T_{e})}{u_{j-1}(T_{e})} \left(\frac{2\pi mk}{h^{2}}\right)^{3/2} T_{e}^{3/2} \exp\left(-\frac{\chi_{j}}{kT_{e}}\right) \ (j = 1, \dots, I_{\max}),$$

which coincide with the Saha equations upon substitution of the electron temperature  $T_e$ . This problem has been examined by Monti and Napolitano [4] for a singly ionized plasma. Their initial assumptions basically coincide with those made above. The absence of conclusions and a final result in [4] makes a detailed comparison impossible.

The derivation of relations (1) is analogous to the derivation of the equilibrium conditions in a one-temperature, chemically reacting mixture with considerable differences in the individual reaction rates. It is important, however, that in this case the conditions of partial equilibrium can be obtained not only by the method used above but also by considering the changes in free energy at constant temperature and volume of the closed system. In our case we cannot use this method owing to the presence of two temperatures. Equations (1) together with the expressions

$$n = \sum_{j=0}^{j_{\max}} n_j, \qquad n_e = \sum_{j=1}^{j_{\max}} j n_j$$

determine the plasma composition as a function of T,  $T_{e^*}$  and the total concentration of heavy particles n or density  $\rho = Mn$ . The addition of the equation of state

$$p = k \left( nT + n_e T_e \right)$$

makes it possible to find the plasma composition as a function of T,  $\rm T_{e^{*}}$  and the total pressure p.

In conclusion, we shall briefly consider the significance of a number of assumptions and some cases where they are inappropriate. It is clear that the fact that the system is adiabatic and closed and the fact that its volume is constant do not number among the assumptions, and, as in ordinary thermodynamics, are necessary only for deriving the required relations. Therefore (1) is equally valid whether or not these conditions are satisfied. The satisfaction of the other conditions, however, is essential. In particular, this applies to the equality of the temperatures of the electron gas and the electron levels of atoms and ions. Failure to observe this condition leads to a change in the equation obtained. In a number of problems, for example, in astrophysics, it is not possible to ignore the effect of radiation. Here, Elwert's results [5] should be used in place of (1). Violation of the assumed relations between the characteristic times of the various processes and the time of each specific problem is general in nature. If the change in the parameters of the problem is as rapid as the processes of change of composition, then the differential equations of chemical kinetics must be solved to determine the composition. Finally, if the change in the parameters of the problem is more rapid than the rate at which equilibrium is established within the chosen subsystems, then to describe their thermodynamic state the differential and integro-differential equations giving the populations of the different electron levels, the composition, and the necessary distribution functions should be used. It is clear that these cases lie outside the range of conditions considered in this article.

## REFERENCES

1. W. F. Westerdorp, C. M. Bishop, H. Hurwitz, L. M. Coldman, and D. J. Ben Daniel, "Nonthermal ionization in transient helium-cesium discharges," Phys. Fluids, vol. 4, no. 6, pp. 786-787, 1961.

2. D. J. Ben Daniel and S. Tamor, "Theory of nonthermal ionization in cesium discharges," Phys. Fluids, vol. 5, no. 4, pp. 500-501, 1962.

3. D. J. Ben Daniel and C. M. Bishop, "Nonequilibrium ionization in a high-pressure cesium-helium transient discharge," Phys. Fluids, vol. 6, no. 2, pp. 300-306, 1963.

4. R. Monti and L. G. Napolitano, 'Influence of excited atoms on the Saha equation for two-temperature plasmas, " Paper read at the XV International Astronautical Congress, Warsaw, September 1964.

5. G. Elwert, "Über die Ionizations und Recombinationsprozesse in einem Plasma und die Ionizationsformel der Sonnenkorona, "Z. Naturforsch, vol. 7, no. 6, pp. 432-439, 1952.

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