DETERMINATION OF THE COMPOSITION OF MULTITEMPERATURE GAS MIXTURES

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Of great interest in the investigation of chemically reacting gas mixtures are those cases in which the forward and reverse reactions are much more rapid than the changes in the thermodynamic parameters of the system. In such cases the concentrations of the components can be found more accurately from finite relationships based on the assumption of chemical equilibrium than from the solution of the equations of chemical kinetics. For single-temperature mixtures such relationships are well known and are formulated either as conditions for maximum entropy S at constant volume V, internal energy E, and mass of the system, or as conditions for minimum free energy F at constant mass, volume, and temperature of the system. These conditions are equivalent, i. e., lead to the same equations.

Owing to the different mechanisms of supplying energy to different particles (electrons and ions, for instance) and to the different degrees of freedom of the same particles, their temperatures can differ appreciably. This difference is particularly great if the mechanisms of interaction of these subsystems do not ensure rapid energy transfer. Such a situation is encountered, for instance, in a plasma, where there may be a considerable difference in the translational temperatures of electrons and ions owing to the great difference in their masses.

If the equalization of the temperatures of the subsystems, like the changes in other thermodynamic parameters, is much slower than the forward and reverse reactions, then the determination of the concentrations can be based on the assumption of partial thermodynamic equilibrium, which means equilibrium with regard to composition, but not with regard to temperature.

It is clear that equations which are valid for complete thermodynamic equilibrium cannot be used for the investigation of multitemperature systems or, at least, will require appropriate modification. A modification of this kind was made in [1–4] for the case of a two-temperature plasma. It has been shown, first from qualitative considerations [1, 2], and then by the thermodynamic approach supplemented with some physically justified assumptions [3, 4], that the equations for the electron and ion concentrations are the same as the equations which hold for complete thermodynamic equilibrium (Saha formulas), if the temperature in them is the temperature of the electron gas. If the conditions formulated in [4] for the role of particular ionization and recombination mechanisms are fulfilled the same result can be derived from the more general formula obtained in [5] on the assumption of detailed balance. The conclusion agrees with the available experimental data [1, 5–7].

It is characteristic of the investigated case that ionization and recombination are energetically connected only with electrons (free electrons or the electron shells of ions) and, hence, have practically no effect on the temperature of the translational degrees of freedom of heavy particles. There can be more complex systems in which different groups of reactions are connected energetically with different subsystems of particles of their degrees of freedom. Below we extend the application of the thermodynamic approach used earlier for a two-temperature plasma [4] to the case of such systems.

It should be noted that in the consideration of multitemperature mixtures erroneous conclusions result from the use of the condition of minimum free energy. The fact is that for single-temperature mixtures this condition, being equivalent to the condition of maximum entropy, leads to a simpler way of obtaining the required relationships. There is thus a temptation to use the same condition for a multitemperature system, for which it has not only not been proved, but is simply untrue. This is clearly demonstrated by the fact that its use for the determination of concentrations gives relationships which differ from those obtained from the condition of maximum S. Yet the correctness of the latter is beyond question, since it follows from the general thermodynamic principle of the direction of change of entropy of an arbitrary adiabatically isolated closed system.

What has been said accounts, in particular, for the incorrectness of [8], where an error was made in an attempt to prove the condition of minimum F. This error consisted in the incorrect expression of the first and second laws of thermodynamics for open subsystems comprising a reacting mixture. The correct expression of these laws with the openness of the subsystems due to the chemical reactions taken into account does not lead to the conclusion made in [8], and merely gives a relationship between the increment F and the increments of the concentrations (at constant V, mass of whole system, and temperature of subsystems).

The thermodynamic approach which can be used to obtain the conditions of chemical equilibrium in a multitemperature mixture can be illustrated by the two-temperature case.

Let the system formed by a reacting mixture be divided into two subsystems within which there is thermodynamic equilibrium. We denote the temperatures of the subsystems by $T^{(1)}$ and $T^{(2)}$. In view of the principle on which the division is based the different subsystems can include not only particles of different gases, but also different degrees of freedom of the same component. For instance, in the case considered in [4] one subsystem was formed by the translational degrees of freedom of heavy particles, and the other consisted of free and bound electrons.

In the considered mixture there occur chemical reactions in which the composition changes and energy is released or absorbed. We will confine ourselves to the case where all the reactions can be divided into two groups such that the reactions of the first (second) group are connected energetically only with the first (second) subsystem. The composition of the mixture is completely determined by specifying the concentrations of all the components. The concentrations of some of the components can be expressed in terms of the concentrations of the others from finite relationships expressing the laws of conservation of chemical elements and charge. If these laws exclude all the superfluous concentrations the condition of constancy of the mass of the closed system will be fulfilled automatically for any changes in the concentration of the remaining components.

The number n of independent concentrations is determined uniquely, but they themselves can be selected in different ways. We will take them so that the concentrations of the first k components vary only as a result of reactions of the first group and the concentrations of the remaining l as a result of reactions of the second group. We denote the corresponding concentrations (number of particles in unit volume) by $n_1^{(1)}, \ldots, n_k^{(1)}$ and $n_1^{(2)}, \ldots, n_l^{(2)}$, and $k + l = n$. These concentrations, together with the volume V occupied by the mixture and the temperatures $T^{(1)}$ and $T^{(2)}$, completely define the thermodynamic state of the considered system, particularly its internal energy and entropy. Hence, we can write

$$E = E(V, T^{(1)}, T^{(2)}, n_1^{(1)}, \ldots, n_k^{(1)}, n_1^{(2)}, \ldots, n_l^{(2)})$$
$$S = S(V, T^{(1)}, T^{(2)}, n_1^{(1)}, \ldots, n_k^{(1)}, n_1^{(2)}, \ldots, n_l^{(2)}) \qquad (1)$$

where the expressions on the right side are known functions of their arguments. The form of these expressions conforms to the general rules of thermodynamics and statistical physics.

We consider the change in entropy which may occur when the composition of a mixture contained in an adiabatically isolated vessel of constant volume changes, i. e., we find the variation in entropy δS in terms of the variation in the concentrations and temperatures when $\delta V = \delta E = 0$.

According to Eq. (1)

$$\delta S = S_T^{(1)}\delta T^{(1)} + S_T^{(2)}\delta T^{(2)} + \sum_{j=1}^{k} S_j^{(1)}\delta n_j^{(1)} + \sum_{j=1}^{l} S_j^{(2)}\delta n_j^{(2)}$$

$$(S_T^{(i)} = \partial S / \partial T^{(i)},\quad S_j^{(i)} = \partial S / \partial n_j^{(i)}). \qquad (2)$$

The variations $\delta T^{(i)}$ and $\delta n_j^{(i)}$ contained in Eq. (2) are not independent, but are connected by the condition $\delta E = 0$, which, in view of Eq. (1), has the form

$$\delta E^{(1)} + \delta E^{(2)} = 0,$$

$$\delta E^{(1)} = E_T^{(1)}\delta T^{(1)} + \sum_{j=1}^{k} E_j^{(1)}\delta n_j^{(1)},$$

$$\delta E^{(2)} = E_T^{(2)}\delta T^{(2)} + \sum_{j=1}^{l} E_j^{(2)}\delta n_j^{(2)}, \qquad (3)$$

where $E_T^{(i)}$ and $E_j^{(i)}$ are determined in a similar way to $S_T^{(i)}$ and $S_j^{(i)}$.

According to the division into subsystems and the choice of independent components, the variations of the quantities with superscripts (1) and (2) are not connected. Hence, equality (3) can be divided into two: $\delta E^{(1)} = 0$ and $\delta E^{(2)} = 0$, and variations $T^{(1)}$ and $T^{(2)}$ can be expressed in terms of the variations $\delta n_1^{(1)}, \ldots,$ and $\delta n_1^{(2)}, \ldots, \delta n_l^{(2)}$, respectively. Substituting the expressions for $\delta T^{(i)}$ in Eq. (2) we obtain δS as a linear form of the variations of the n independent concentrations.

Since the entropy of a system contained in an adiabatically isolated vessel of constant volume can only increase, its value will be a maximum in the state of chemical equilibrium. Hence, in view of the independence of $\delta n_j^{(1)}$, we find that the conditions which determine the composition of the mixture have the form

$$S_j^{(1)} - S_T^{(1)}(E_j^{(1)}/E_T^{(1)}) = 0 \qquad (j = 1, \ldots, k)$$
$$S_j^{(2)} - S_T^{(2)}(E_j^{(2)}/E_T^{(2)}) = 0 \qquad (j = 1, \ldots, l).$$

Substituting in the functions on the left side their expressions calculated in accordance with Eq. (1) we obtain n equations, from which we can find expressions for all the concentrations as functions of $T^{(1)}$, $T^{(2)}$, and V.

The discussed approach is valid in the case of complete thermodynamic equilibrium too. Here, however, Eq. (3) is not divided into two and, hence, in the expression for δS we can eliminate only one temperature. Accordingly, to Eqs. (4) we add another equation

$$S_T^{(2)}E_T^{(1)} - S_T^{(1)}E_T^{(2)} = 0$$

which for all specific cases means equality of the temperatures, as must be the case in complete thermodynamic equilibrium. Thus, in the adopted approximation, as in the case of a two-temperature plasma, the equations giving the concentrations in terms of the volume and temperature differ from the equilibrium relationships solely in the replacement of the over-all temperature by the temperatures of the different subsystems (these equations can contain several temperatures). This result still holds in the case of a multitemperature mixture.

The obtained formulas are approximate. Their accuracy increases with increase in the ratio of the rates of the forward and reverse reactions to the rates of equalization of the temperatures and change in the thermodynamic parameters of the mixture. We will characterize this ratio by the parameter r. Then formulas (4) can be used only if

$$r \gg 1 \qquad (5)$$

and when r → ∞ these formulas become exact. Condition (5) is essential also for the validity of the more exact relationships which can be obtained from the condition of quasi stationarity by using either the condition of detailed balance (5) or the principle of minimum entropy production [9]. The range of applicability of the more accurate formulas is also a little greater. However, to write these equations we require, in addition to the constants contained in Eqs. (4), a knowledge of additional kinetic coefficients. With reduction in r the error of all these formulas increases and they must be replaced by the differential equations of chemical kinetics.

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