Two-Temperature Saha Equation: A Misunderstood Problem

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Introduction

IN these last years, considerable interest has been devoted to the thermodynamics of multi-temperature gas mixtures, with particular emphasis on the chemical equilibrium of two-temperature partially ionised gases. The solution of this problem was attempted by various authors[1–3] (see the list of references given in Ref. 2) via the minimization of the Helmholtz or Gibbs potentials relative to the plasma mixture, assuming the constancy of the different temperatures as constraints. Such an approach leads to the most used two-temperature Saha equation. However, Morro and Romeo[4] have analyzed the problem in a fluid dynamics context; the two-temperature Saha equation they obtain derives from the imposition of the vanishing of the chemical reaction rates (see Sec. 4 of Ref. 4), but its mathematical structure differs from the equation derived in a pure thermodynamic context.[1,2] A two-temperature Saha equation similar in structure to the one proposed by Morro and Romeo was also derived on grounds of more thermodynamic nature by Van de Sanden et al.[5] and by Van de Sanden.[6] The existence of these nonequivalent equations has generated some confusion in the literature, as pointed out recently by Mertogul and Krier.[7]

The purpose of this Note is to show that the apparent contradiction can be explained in the framework of the thermodynamics of multitemperature systems as developed by Napolitano,[8] and, recently, re-examined and completed by one of the present authors.[9]

Analysis

We consider a gas mixture composed by atoms A, ions A^+, and electrons e^-, subjected to the chemical reaction

$$A \rightleftharpoons A^+ + e^- \tag{1}$$

and we assume that the degrees of freedom or energy modes, of atoms and ions are in mutual thermal equilibrium; consistently, atoms and ions share the same temperature T_h, whereas the electrons have a different temperature T_e. It is worth noticing that such an assumption may not accurately reflect the recent experimental findings relative to atoms and ions having their electronic excitation temperatures different from their translational temperatures; however, this fact is irrelevant in the context of the present analysis. A more general treatment relative to the thermodynamic equilibrium of multitemperature gas mixtures that accommodates for any number of different temperatures and chemical reactions is given by Giordano.[9]

The fundamental relations[8] for energy and entropy describing the thermodynamics of the considered system read, respectively,

$$U = U(S_h, S_e, V, N_A, N_{A^+}, N_e) \tag{2}$$

$$S = S(U_h, U_e, V, N_A, N_{A^+}, N_e) \tag{3}$$

In Eqs. (2) and (3), S_h is the sum of the entropies of atoms and ions, S_e is the entropy of the electrons, V is the volume, U_h is the sum of the energies of atoms and ions, U_e is the energy of the electrons, and the N_i are the mole numbers of the species. The fundamental relations (2) and (3) are perfectly equivalent. Analogously, the Helmholtz and Gibbs potentials read

$$F = F(T_h, T_e, V, N_A, N_{A^+}, N_e) \tag{4}$$

$$G = G(T_h, T_e, p, N_A, N_{A^+}, N_e) \tag{5}$$

In Eq. (5), p denotes the thermodynamic pressure.

The most popular two-temperature Saha equation can be obtained from the minimization of the function U, provided that the entropies S_h, S_e, and the volume V are kept constant; this is also equivalent to minimize the functions F or G, but keeping constant the temperatures T_h, T_e, and the volume V or the pressure p, respectively. In fact, under the assumed constraints, the differentials of those functions read

$$\begin{aligned}(\mathrm{d}U)_{S_h,S_e,V} &= (\mathrm{d}F)_{T_h,T_e,V} = (\mathrm{d}G)_{T_h,T_e,p} \\ &= (\mu_{A^+} + \mu_e - \mu_A)\,\mathrm{d}\xi\end{aligned} \tag{6}$$

In Eq. (6), the μ_i are the molar chemical potentials of the species, defined as $\mu_i = (\partial U/\partial N_i)_{S_h,S_e,V,N_{j\neq i}}$, and ξ is the progress variable of the reaction (1); the chemical potentials are evaluated at their corresponding temperatures. In conditions of chemical equilibrium

$$\mu_{A^+} + \mu_e - \mu_A = 0 \tag{7}$$

and the substitution of the usual perfect gas expressions of the molar chemical potentials

$$\mu_i = \mu_i^0(T_i) + RT_i \ell n\, p_i \tag{8}$$

into the equilibrium condition (7) leads to the expression

$$p_e(p_{A^+}/p_A)^{T_h/T_e} = \exp[-(\Delta\mu^0/RT_e)] \tag{9}$$

in which $\Delta\mu^0$ is given as

$$\Delta\mu^0 = \mu_{A^+}^0(T_h) + \mu_e^0(T_e) - \mu_A^0(T_h) \tag{10}$$

The two-temperature Saha equation similar in structure to the one proposed by Morro and Romeo can be obtained from the maximization of the function S provided that the energies U_h, U_e, and the volume V are kept constant. When account is taken of the following definition:

$$\frac{\mu_i}{T_i} = -\left(\frac{\partial S}{\partial N_i}\right)_{U_h,U_e,V,N_{j\neq i}} \tag{11}$$

and of the assumed constraints, the differential of the entropy S reads

$$(\mathrm{d}S)_{U_h,U_e,V} = -\left(\frac{\mu_{A^+}}{T_h} + \frac{\mu_e}{T_e} - \frac{\mu_A}{T_h}\right)\mathrm{d}\xi \tag{12}$$

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The condition governing the chemical equilibrium becomes

$$\frac{\mu_{A^+}}{T_h} + \frac{\mu_e}{T_e} - \frac{\mu_A}{T_h} = 0 \tag{13}$$

The substitution of the expression (8) into Eq. (13) leads to the expression

$$\frac{p_e p_{A^+}}{p_A} = \exp\left(-\frac{\Delta\mu^\circ}{RT_h}\right) \exp\left(-\frac{T_h - T_e}{T_h T_e}\,\mu_e^\circ\right) \tag{14}$$

The major differences between Eq. (9) and Eq. (14) are 1) the appearance of the exponent T_h/T_e relative to the partial pressure ratio p_{A^+}/p_A in the left-hand side of Eq. (9) and 2) the different combinations of temperatures in the right-hand sides of both equations. As expected, the equations come to coincide in case of thermal equilibrium ($T_h = T_e$).

Conclusions

Equations (9) and (14) are both valid because they correspond to different thermodynamic situations of equilibrium. To this regard, the major role is played by the constraints that are imposed on the gas mixture. The apparent confusion, existing in the literature, disappears when one realizes that the two equations are determined by different constraints. The applicability of each equation depends, therefore, on the particular experimental conditions to which the gas mixture is subjected.

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