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WIEDEMANN-FRANZ RATIO IN PLASMAS IN THE MIXTURES OF XENON, ARGON AND CAESIUM

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Abstract. *In the present paper, the xenon plasmas containing argon and caesium as additive and pertaining to the above mentioned type (high-pressure, low-temperature, LTE) are studied, and a theoretical evaluation of their basic transport parameters is presented. The numerical calculations were based on the assumption that the system is kept under constant pressure and temperature and that it attained local thermodynamical equilibrium. Some results of a theoretical study which embraced numerical evaluations of the plasma composition, electron collision frequency, electrical and thermal conductivities and Wiedemann-Franz ratio, all regarded as functions of pressure and temperature, are given for high-pressure (from 0,1 MPa to 1,5 MPa) and low-temperature (from 2 000 K to 20 000 K). A previously derived modified expression for the Debye radius, offering the possibility to treat the plasmas considered as weakly non-ideal in the whole temperature range of interest, is used in the evaluations, in combination with the Saha equations for the relevant ionization stages of xenon, argon and caesium.*

Key words: *xenon plasma, argon, caesium, local thermodynamical equilibrium, number density, collision frequency, electrical conductivity, thermal conductivity, Wiedemann-Franz ratio.*

1. INTRODUCTION

Some noble-gases such as He, Ne, Ar, Kr, Xe and mixtures with some gases, such as alkaline vapours are important in practical applications, such as electrical discharge engineering the development or radiation detectors, gas lasers and plasma technology. Plasmas in mixtures of noble and other gases are of considerable interest from the mixtures of noble gases and caesium, in particular, are also of importance in different laboratory situations. The basic characteristics of these plasmas in the investigation are the number densities of their constituents and transport coefficients. Unfortunately, results of direct experimental measurements of these basic parameters are not always available, especially in the above conditions.

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In this paper the results of a theoretical evaluation of equilibrium plasma composition, electrical conductivity, thermal conductivity and their ratio (the Wiedemann-Franz ratio) in xenon plasma with 10% of argon and 10% of caesium are presented, for the temperature range from 2 000 K to 20 000 K, and for pressures equal to or 5, 10, and 15 time higher than the normal atmospheric pressure. The plasma was regarded as weakly non-ideal and in the state of the local thermodynamical equilibrium (LTE) with the assumption that the equilibrium is attained with the pressure kept constant. This evaluation procedure was already introduced in studies of noble gas plasmas with alkaline vapours (or chlorine and fluorine) as additive [1-8].

2. OUTLINE OF THE THEORY

To determine the transport characteristics in plasmas formed mixtures of noble-gases and alkaline vapour, it is necessary to evaluate the equilibrium plasma composition and the electron-atom, electron-ion and electron-electron collision frequencies. In the evaluations given below, it was assumed that, apart from the atoms of noble-gases and caesium, as well as the ions of ehese elements obtained as a result of process of the first and second thermal ionizations. Thus, including the electrons, a total of 10 sorts of particles were taken into account:

$$\begin{matrix} \mathrm{e}, & \mathrm{Xe}, & \mathrm{Ar}, & \mathrm{Cs}, & \mathrm{Xe}^{+}, & \mathrm{Ar}^{+}, & \mathrm{Cs}^{+}, & \mathrm{Xe}^{++}, & \mathrm{Ar}^{++}, & \mathrm{Cs}^{++} \\ n_e, & n_{10}, & n_{20}, & n_{30}, & n_{11}, & n_{21}, & n_{31}, & n_{12}, & n_{22}, & n_{32} \end{matrix}$$

Therefore, the plasma composition was evaluated from the following set of equations

$$n_{11} + 2\,n_{12} + n_{21} + 2\,n_{22} + n_{31} + 2\,n_{32} = n_e; \tag{1}$$

$$n_{10} + n_{11} + n_{12} = \frac{p}{(1+\alpha_1+\alpha_2)kT_0} \tag{2a}$$

$$n_{20} + n_{21} + n_{22} = \frac{\alpha_1 p}{(1+\alpha_1+\alpha_2)kT_0} \tag{2b}$$

$$n_{30} + n_{31} + n_{32} = \frac{\alpha_2 p}{(1+\alpha_1+\alpha_2)kT_0} \tag{2c}$$

$$\frac{n_{11}n_e}{n_{10}} = K_{11},\ \frac{n_{12}n_e}{n_{11}} = K_{12},\ \frac{n_{21}n_e}{n_{20}} = K_{21},\ \frac{n_{22}n_e}{n_{21}} = K_{22},\ \frac{n_{31}n_e}{n_{30}} = K_{31},\ \frac{n_{32}n_e}{n_{31}} = K_{32}. \tag{3a-f}$$

Equation (1) is easily identified as the charge–conservation requirement, whereas eqs. (2a), (2b) and (2c) are requirements of conservation of total numbers of xenon, argon and caesium nuclei. The parameters α_1 and α_2 appearing in these equations refers to the contamination; α_1 is the ratio of initial number densities of argon and xenon neutral atoms, α_2 is the ratio of the initial number densities of caesium and xenon neutral atoms at the initial temperature T_0. Equations (3a-f) express the law of mass action applied to the two ionization stages of noble-gases and caesium. In view of the assumed LTE, the equilibrium constants in these equations will be taken in the simple Saha-Eggert form

$$K_{11} = C\frac{g_{11}^0}{g_{10}^0}\exp(-\frac{W_{10}-\Delta W^{(1)}}{kT}), \quad (4a) \qquad K_{12} = C\frac{g_{12}^0}{g_{11}^0}\exp(-\frac{W_{11}-\Delta W^{(2)}}{kT}), \quad (4b)$$

$$K_{21} = C\frac{g_{21}^0}{g_{20}^0}\exp(-\frac{W_{20}-\Delta W^{(1)}}{kT}), \quad (4c) \qquad K_{22} = C\frac{g_{22}^0}{g_{21}^0}\exp(-\frac{W_{21}-\Delta W^{(2)}}{kT}), \quad (4d)$$

$$K_{31} = C\frac{g_{31}^0}{g_{30}^0}\exp(-\frac{W_{30}-\Delta W^{(1)}}{kT}), \quad (4e) \qquad K_{32} = C\frac{g_{32}^0}{g_{31}^0}\exp(-\frac{W_{31}-\Delta W^{(2)}}{kT}). \quad (4f)$$

Here, $C = 2(2\pi m_e kT / h^2)^{3/2}$, g_{ij}^0 are the multiplicities (degeneracies) of the lowest energy levels of the corresponding atomic species (i = 1,2,3; j = 1,2), W_{10}, W_{20} and W_{30} are the energies of the first ionization ($A \rightarrow A^+$) respectively for xenon, argon and caesium, W_{11}, W_{21} and W_{31} are the corresponding energies for the second ionization ($A^+ \rightarrow A^{++}$) and

$$\Delta W^{(i)} = \frac{i}{4\pi\varepsilon_0}\frac{e^2}{\dot{r}_d}, \quad (i = 1,2) \tag{5}$$

are the effective energy lowerings for the two ionization stages taken into account in this work. The modified plasma Debye radius $\overset{*}{r}_D$ (rather than the standard r_D), as proposed previously [1,2,4].

The electrical and thermal conductivities were evaluated according to the formulae [9,10]

$$\sigma = \frac{2e^2 n_e}{3\sqrt{2\pi}} m_e^{3/2} (kT)^{-5/2} \int_0^\infty \frac{v^4}{\nu_e(v)} \exp\left(-\frac{m_e v^2}{2kT}\right) dv\,, \tag{6}$$

$$\lambda = \frac{n_e}{3\sqrt{2\pi}T} m_e^{5/2} (kT)^{-3/2} \int_0^\infty \frac{v^6}{\nu_e(v)} \left(\frac{m_e v^2}{2kT} - \frac{5}{2}\right) \exp\left(-\frac{m_e v^2}{2kT}\right) dv\,, \tag{7}$$

valid if the electrons possess the velocity distribution function with a Maxwellian isotropic part, which is compatible with the assumed existence of the LTE.

The overall frequency of the electron elastic collisions is taken in its usual form

$$\nu_e(v) = 2\pi v \sum_\alpha n_\alpha Q_{e\alpha}(v)\,, \tag{8}$$

with $Q_{e\alpha}$ standing for the effective velocity-dependent cross sections for elastic scattering of electrons on the particles of the species α, n_α being the corresponding number densities (summation with respect to the index α in (8) is taken over all the species present, including the electrons). In the present work, the collisions with the ions were described by the Spitzer-Härm formula, and those with the neutrals are accounted for by polynomial formulae interpolating selected sets in the form gives in [1]. Electron-electron collision frequency was based on the well-known expression $\nu_{ee} \approx \sqrt{2}\ \nu_{ei}$ [11].

3. RESULTS AND COMMENTS

The number densities of electrons and ions tend to increase with the temperature, and one can easily grasp the significance of the relations between the ionization energies of the neutral species present.

Figure 1. shows the temperature dependence of the evaluated electrical conductivity σ^* (the asterisk indicating the use of r_D^* instead of r_D), with pressure as parameter, for the composite plasma considered here. It is clearly seen that, below some 6 000 K, the electrical conductivity is virtually independent of the pressure, and that it increases with the pressure above that temperature. This trait is amenable to the added caesium, since in both pure xenon and pure argon a decrease of electrical conductivity with the pressure ($\sigma^* \sim p^{-1/2}$) is found [1,2,5,6]. Although the variations of n_e are basic importance, the inclusion of electron-atom collisions is also quite significant in establishing the features shown in Fig.1.

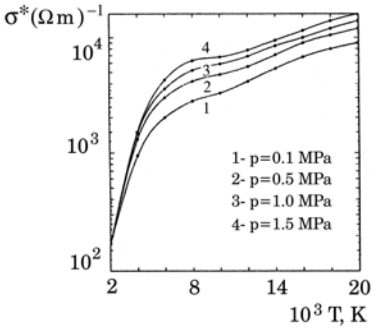

Fig. 1. Electrical conductivity in xenon plasma with 10% argon and 10% caesium

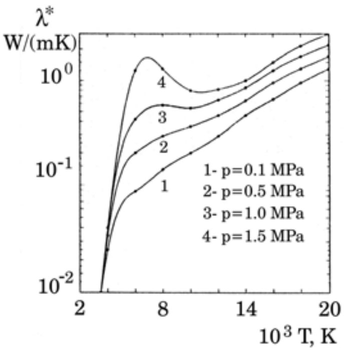

Fig. 2. Thermal conductivity in xenon plasma with 10% argon and 10% caesium

Figure 2. shows the temperature dependence of the evaluated thermal conductivity λ^*. Much as in the case of σ^*, the calculated values of λ^* are virtually independent of the pressure at lower temperatures (below some 4 000 K). At higher temperatures, the increase of λ^* with the pressure becomes quite noticeable, even more remarkable that in σ^*. Again, this is primarily ascribable to the variations in n_e due to the presence of caesium, although the inclusion of electron-atom collisions provides a non-negligeable contribution as well.

Finally, Fig. 3 shows the temperature dependence of the ratio λ^*/σ^*, again with the pressure as parameter. The unusual feature to be seen in this Fig. is that, much like σ^* and λ^*, this ratio varies with the pressure, increasing if the pressure is raised. However, this cannot be ascribed to the presence of the alkaline additive, as the electron number densities cancel out in forming the ratio of (6) and (7) under the assumption that $\nu_e = const.$ It can be inferred that the electron-atom collisions have the largest influence, in the case studied, between 5 000 K and 10 000 K.

Table 1. Electron number densities and collision frequencies in xenon plasma with 10% argon and 10% caesium

T, K	n_e, m^{-3}	ν_{ea}, s^{-1}	ν_{ei}, s^{-1}	ν_{ee}, s^{-1}
2 000	$7{,}4 \times 10^{20}$	$4{,}0 \times 10^{12}$	$1{,}7 \times 10^{11}$	$2{,}5 \times 10^{11}$
4 000	$3{,}8 \times 10^{23}$	$1{,}7 \times 10^{12}$	$1{,}2 \times 10^{13}$	$1{,}7 \times 10^{13}$
6 000	$1{,}9 \times 10^{24}$	$9{,}9 \times 10^{11}$	$2{,}8 \times 10^{13}$	$3{,}9 \times 10^{13}$
8 000	$2{,}4 \times 10^{24}$	$1{,}2 \times 10^{12}$	$3{,}0 \times 10^{13}$	$4{,}2 \times 10^{13}$
10 000	$2{,}6 \times 10^{24}$	$1{,}7 \times 10^{12}$	$2{,}8 \times 10^{13}$	$3{,}9 \times 10^{13}$
12 000	$3{,}8 \times 10^{24}$	$2{,}4 \times 10^{12}$	$3{,}2 \times 10^{13}$	$4{,}6 \times 10^{13}$
14 000	$6{,}9 \times 10^{24}$	$2{,}8 \times 10^{12}$	$4{,}5 \times 10^{13}$	$6{,}3 \times 10^{13}$
16 000	$1{,}1 \times 10^{25}$	$2{,}8 \times 10^{12}$	$5{,}8 \times 10^{13}$	$8{,}2 \times 10^{13}$
18 000	$1{,}6 \times 10^{25}$	$2{,}4 \times 10^{12}$	$5{,}8 \times 10^{13}$	$9{,}6 \times 10^{13}$
20 000	$1{,}9 \times 10^{25}$	$1{,}9 \times 10^{12}$	$7{,}3 \times 10^{13}$	$1{,}0 \times 10^{14}$

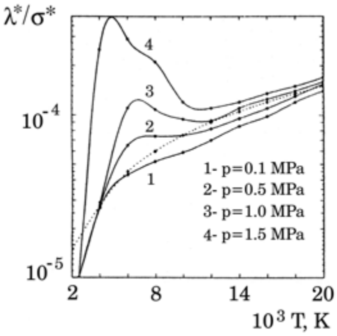

Fig. 3. Franz-Wiedemann ratio in xenon plasma with 10% argon and 10% caesium

The results of the numerical evaluations of the electron collision frequencies are given in Tab. 1. This Table show the relative role of the electron-atoms collisions. The influence of ν_{ea} decreases as the temperature increases, but increases if the pressure is raised. Electron-atoms collision frequency at lower temperatures is larger than the total collisions frequency of electrons with the charged particles (electron-ion and electron-electron) up to 6 000 K, where one has $\nu_{ea} \approx \nu_{ei} + \nu_{ee}$; this holds approximately up to the 8 000 K or 10 000 K depending on the percentage of caesium. At higher temperatures the ratio $\nu_{ea} / \nu_{ei} + \nu_{ee}$ is smaller than unity. This ratio varies slowlies with the pressures.

4. CONCLUSION

It can be, thus, concluded that the increase of the raises electron collision frequencies at temperatures up to some 12 000 K in plasmas with caesium added basically consequence of the increase of the electron number densities.

The obtained values for n_e led to conclusion that the assumption on the local thermodynamical equilibrium was well met in both plasmas. In the argon plasma it is generally accepted [12] that LTE exists if $n_e \geq 5 \times 10^{21}$m^{-3}, and this was found to be valid within the whole temperature range considered and for all the pressures taken into account.

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WIEDEMANN-FRANZ -OV ODNOS U PLAZMI SMEŠE KSENONA, ARGONA I CEZIJUMA

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Dati su rezultati izračunavanja osnovnih transportnih parametara u plazmi ksenona sa dodatkom argona i cezijuma. Numerička izračunavanja se zasnivaju na činjenici da je sistem na konstantnom pritisku i konstantnoj temperaturi u stanju lokalne termodinamičke ravnoteže. Dati su neki rezultati o ravnotežnom sastavu, kolizionoj frekvenci, električnoj i toplotnoj provodljivosti i Wiedemann-Franz-ovom odnosu za visoke pritiske (0,1 Mpa –1,5 MPa) i za niske temperature (2 000 K - 20 000 K). Korišćen je izraz za modifikovan Debye-ev radijus, čime je zadovoljen uslov slabe neidealnosti u ukupnom temperaturnom intervalu, u kombinaciji sa Saha-ovim jednačinama za odgovarajuća jonizaciona stanja ksenona, argona i cezijuma.