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Calculation of diffusion coefficients in air-metal thermal plasmas

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Abstract : This paper presents the combined diffusion coefficients of metal vapours (silver, copper and iron) in air thermal plasmas for temperatures ranging from 300 to 30000K. The theory used to calculate these coefficients is remembered and validated by comparison with literature values in several cases such as Ar-He, Ar-Cu and N₂-O₂ mixtures. The results are discussed showing the influences of the metal concentration, of the vapour nature and of the pressure. The results show rather similar behaviour for the three metals. The maximum values of the combined ordinary diffusion coefficient in the evolution with temperature, is obtained for temperature around 10 000K but this peak is shifted to the highest temperatures when the metal proportion increases. Another result shows that the diffusion coefficient decreases when pressure increases.

Keywords : diffusion, thermal plasmas properties, air, copper, silver, iron,

1. Introduction

In Industry, most of plasma processes use complex gas mixtures. For switching arcs for example, we can find sulphur hexafluoride, nitrogen or air mixed together with metallic, organic (PA66, PMMA, PTFE) vapours resulting from the erosion of the walls and/or contacts. Other mixtures based on argon, helium, hydrogen, nitrogen, oxygen or carbon dioxide with or without metallic vapours are often used for welding, cutting, surface treatment, spraying or engraving techniques. Finally, more peculiar mixtures are used in plasma torches for waste destruction or fullerenes production.

The development of these processes has a growing importance and the main difficulties in their study have resulted in the considerable increase of numerical modelling. In the great majority of numerical models developed for thermal plasmas, normal diffusion is supposed to be negligible as compared to the turbulent diffusion or to convection. Murphy has shown that this approximation was not always valid even more if demixing phenomenon exists in the plasma [1]. Diffusion is usually due to gradients of densities, of temperatures, of pressure and external forces (friction forces or electrical field for examples). Moreover, these different phenomena can exist simultaneously. The consequence is that species can be separated in the plasma leading to departures from chemical equilibrium. Therefore, it becomes very difficult to interpret the diffusion which may constitute the main cause of departures from equilibrium in thermal plasmas.

To treat the diffusion phenomena in the numerical models, we have to calculate the ordinary diffusion coefficients. Those coefficients constitute a major problem because they are too numerous to be implemented in a numerical model. For a plasma containing Q species, we must determine $Q(Q-1)/2$ ordinary diffusion coefficients. Several authors have simplified the problem by introducing specific diffusion coefficients, describing the diffusion of all the species of a gas in comparison to those of the other one. Among the various approximations or combinations of the diffusion coefficients [2,3,4], Murphy has developed an interesting concept which consists of a combination of diffusion flux which enables us to define a combined diffusion coefficient [5]. The advantage of this method lies in the fact that this coefficient is independent of the number of chemical species and it only depends on the elementary constituents present in the plasma. The diffusion is then taken into account through only one diffusion coefficient. However, this method can only be applied to binary mixtures, for homo-nuclear and non-reactive gases.

Because of the strong interaction between the arc and the electrodes (or contacts) several kinds of arc applications or systems lead to the production of thermal plasmas established in a mixture of air with metallic vapours: low voltage circuit-breakers, cutting arcs in air, Laser Induced Breakdown Spectroscopy, effect of lightning on materials. This paper is devoted to the study of the diffusion in air plasmas in presence of metallic vapours; nevertheless some results on argon containing mixtures and on N_2-O_2 mixtures will be presented to propose some validation and comparison with literature and to allow some general conclusions. After the presentation of the method used to calculate the combined diffusion coefficients, we will give some results of these coefficients due to gradients of concentration and gradients of the electrical field, for 3

metals: iron, copper and silver. The temperature and pressure ranges used for these calculations correspond to the ranges covering the conditions for a lot of thermal plasma applications including low voltage circuit breaker arcs. The lowest value of pressure is 0.5 bar because some underpressure effect may occur in particular applications. We may consider that the pressure limits for thermal plasmas are 0.1 bar (severe departures from equilibrium may occur at lowest pressures) and a few tens of bars where non-ideal effects may change the plasma composition.

2. Theory

2.1. General expressions

Diffusion is mainly due to gradients of particle number densities. But, a gradient of temperature can modify a flux of particles (Soret effect), while a gradient of concentration can cause an energy flux (Duffour effect) and the particle flux may also be influenced by a pressure gradient and by external forces. Therefore, for a given species i in a mixture containing q species, Hirschfelder [4], Devoto [6], Chapman and Cowling [7] and Murphy [5;8] write the particle flow as:

$$\begin{aligned}
 \vec{g}_i \equiv n_i \vec{v}_i = & \frac{n^2}{\rho} \sum_{j=1}^q m_j D_{ij} \vec{\nabla} x_j \\
 & + \frac{n^2}{\rho} \sum_{j=1}^q m_j D_{ij} \left(x_j - \frac{\rho_j}{\rho} \right) \vec{\nabla} \ln P \\
 & - \frac{n^2}{\rho} \sum_{j=1}^q m_j D_{ij} \frac{\rho_j}{P\rho} \left[\frac{\rho}{m_j} \vec{F}_j - \sum_{\ell}^q n_{\ell} \vec{F}_{\ell} \right] \\
 & - \frac{D_i^T}{m_i} \vec{\nabla} \ln T
 \end{aligned} \tag{1}$$

where n and n_i are the total number density and the number density of species i respectively ($i=1$ for electrons), m_i the mass of i particles, \vec{v}_i the mean velocity of i particles, ρ and ρ_i are the total mass density and the mass density of species i expressed in kg/m^3 . x_i is the mole fraction of the species i and P is the pressure. F_i is a force applied on particles i . D_{ij} are ordinary diffusion coefficient of species i in species j , and D_i^T the thermal diffusion coefficient of species i . In literature several expressions are proposed to compute the D_{ij} coefficients. In our case they have been calculated using the general expression recommended by Rat et al [8] and previously given by Devoto [6] up to the order 4 of the Chapman-Enskog theory:

$$[D_{ij}]_a = \frac{3\rho n_i}{2nm_j} \left(\frac{2\pi kT}{m_i} \right)^{1/2} \begin{array}{cccc|c} [q_{hk}^{00}] & [q_{hk}^{01}] & [q_{hk}^{02}] & [q_{hk}^{03}] & \delta_{hj} - \delta_{hi} \\ [q_{hk}^{10}] & [q_{hk}^{11}] & [q_{hk}^{12}] & [q_{hk}^{13}] & 0 \\ [q_{hk}^{20}] & [q_{hk}^{21}] & [q_{hk}^{22}] & [q_{hk}^{23}] & 0 \\ [q_{hk}^{30}] & [q_{hk}^{31}] & [q_{hk}^{32}] & [q_{hk}^{33}] & 0 \\ \hline \overline{\delta_{ki}} & \overline{0} & \overline{0} & \overline{0} & 0 \end{array}$$

with $[q_{hk}^{mp}]$ are composed of q^2 terms q_{ij}^{mp} such as $[q_{hk}^{mp}] \Leftrightarrow \begin{array}{ccc} q_{11}^{mp} & \cdots & q_{1q}^{mp} \\ \vdots & \ddots & \vdots \\ q_{q1}^{mp} & \cdots & q_{qq}^{mp} \end{array}$

$\overline{\delta_{ki}}$ is composed of q terms δ_{ki} : $\overline{\delta_{ki}} \Leftrightarrow \delta_{1i} \cdots \delta_{ki} \cdots \delta_{qi}$

$\overline{0}$ is composed of q zeros: $\overline{0} \Leftrightarrow 0 \cdots 0$

$\delta_{hj} - \delta_{hi}$ corresponds to q terms $\delta_{hj} - \delta_{hi}$: $\begin{array}{c} \delta_{1j} - \delta_{1i} \\ \vdots \\ \delta_{hj} - \delta_{hi} \\ \vdots \\ \delta_{qj} - \delta_{qi} \end{array}$

Murphy [9-11] showed for thermal plasmas that gradients of pressure and gradients of electric field are often weak in comparison with the gradients of densities; and thermal diffusion coefficients are generally lower than ordinary diffusion coefficient. Therefore, the relation (1) can be written more simply [5] as a first approximation:

$$\vec{g}_i = \frac{n^2}{\rho} \sum_{j=1}^q \left[m_j D_{ij}^a \cdot \vec{\nabla} x_j \right] \quad (2)$$

with D_{ij}^a the ordinary diffusion coefficients (corrected with the ambipolar diffusion) calculated according to [5,9]:

$$D_{ij}^a = D_{ij} + \frac{\alpha_i}{\beta} \sum_{\ell=1}^q Z_\ell D_{\ell j} \quad (3)$$

$$\begin{aligned} \alpha_i &= \sum_{j=1}^q n_j m_j Z_j D_{ij} \\ \text{with} & \\ \beta &= -\sum_{i=1}^q \sum_{j=1}^q Z_i Z_j n_j m_j D_{ij} \end{aligned} \quad (4)$$

Z_j is the charge of particle j . For a gas containing several species, these ordinary diffusion coefficients check the following conditions:

$$D_{ii} = 0 \quad \text{and} \quad D_{ij} \neq D_{ji} \quad \text{if} \quad i \neq j \quad (5)$$

According to Murphy, the combined diffusion coefficients $\overline{D_{AB}^x}$ (due to the gradients of densities and called by Murphy “the combined ordinary diffusion coefficients”, CODC) finally can be written as:

$$\overline{D_{AB}^x} = \frac{1}{m_B} \sum_{i=2}^p s_i^A \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_j}{\partial x_B} \quad (6)$$

with

$$\overline{m_B} = \frac{\sum_{i=p+1}^q (m_i x_i + m_1 Z_i x_i)}{\sum_{i=p+1}^q x_i} \quad (7)$$

$$\overline{x_B} = \sum_{i=p+1}^q (1 + Z_i) x_i = 1 - \overline{x_A} \quad (8)$$

$$s_i^A = \frac{b_i \sum_{j=2}^p x_j}{\sum_{j=2}^p b_j x_j} \quad \text{for} \quad 2 \leq i \leq p \quad (9)$$

In relations (6) to (9), A represents the air (or argon) plasma and B the metal vapour, p is the total number of chemical species for the gas A ($p=26$ for air and $p=4$ for argon) and q the total number of species in the mixture ($q=34$ for air-metal, $q=11$ for Ar-metal). The coefficient b_i is the number of atoms constituting the species i ($b_i=1$ for the homonuclear particle and $b_i \geq 2$ for molecules).

Considering the mass flow of the electrons and the fact that the sum of the mass flows is equal to zero, Murphy showed that $\overline{D_{AB}^x} = \overline{D_{BA}^x}$ [12]. In relation (6), we may note the presence of the term $\partial x_j / \partial \overline{x_B}$ which compels us to calculate the plasma composition for higher and lower concentrations and the derivative is computed from $\Delta x_j / \Delta \overline{x_B}$.

In some cases, the diffusion due to the presence of an electric field is not negligible. Consequently, the third term in relation (1) must be calculated. The corresponding combined diffusion coefficients $\overline{D_{AB}^E}$ (due to the gradients of electric field) can be written as [12]:

$$\overline{D_{AB}^E} = -\frac{e}{k_B T} \cdot \frac{1}{m_B} \sum_{i=1}^p s_i^A \sum_{j=1}^q m_j x_j Z_j D_{ij} \quad (10)$$

where k_B is the Boltzmann constant. Murphy showed that $\overline{D_{AB}^E} = -\overline{D_{BA}^E}$.

2.2. Calculation of the ordinary diffusion coefficients (interaction potentials)

According to the relation (3) and (4), the combined diffusion coefficients are strongly influenced by species properties. Consequently, they can be different depending on the interactions taken into account to characterize the collisions in the plasma. These collisions are characterized through functions called collision integrals [4]. The diffusion coefficients are thus functions which strongly depend on the interaction potentials or cross sections chosen to represent the collisions and to calculate the collision integrals. The data necessary to estimate these functions are issued from [13] for Ar-Cu mixtures and [14] for Ar-He mixtures. For the Ar-Fe mixtures, the literature does not give enough data. Therefore, the collision integrals have been calculated according to empirical formula given by Hirschfelder [4]. The latter are defined for several potentials as Lennard-Jones, polarisability or rigid spheres and they cannot be calculated without the knowledge of the parameters reported in table 1.

Table 1. Parameters for theoretical expressions

Species	ϵ/k (K)	σ (Å)	ξ (Å ⁻³)	r_m (Å)
Ar	93.3	3.542	1.6411	1.56
He	10.8	2.576	0.2049	1.40
Fe	3000.0	4.300	8.4000	1.93
Cu	2983.0	5.058	7.3100	1.56

For air-metal mixtures all the interaction potentials and collision integrals are the same used for calculating the other transport coefficients reported in our recent publication [15].

3. Validation and argon-copper results

Figure 1 shows the CODC obtained for Ar-N₂ and Ar-O₂ mixtures (note that in this case the proportions are volumetric or molar). Our results are in good agreement with those of Murphy [5], his results being slightly lower for both mixtures. This difference is due to different values used for the integral collisions. For example in the case of Ar-N₂ mixture, we characterized the Ar-N and Ar-N₂ interactions using a Lennard-Jones potential whereas Murphy used an exponential potential (spline - Morse - spline - Van der Waals). The choice of the interaction potential may influence the results obtained for the combined coefficients of diffusion. In our case we have voluntarily applied the Lennard-Jones potential for Ar-N₂ and Ar-N for 3 reasons:

- it is much easier to use it (for us) than the exponential potential;
- the influence of this choice only concerns the evolution of diffusion at low temperature;
- the purpose was not to obtain in this case the best results but to have rather accurate results to provide an available comparison.

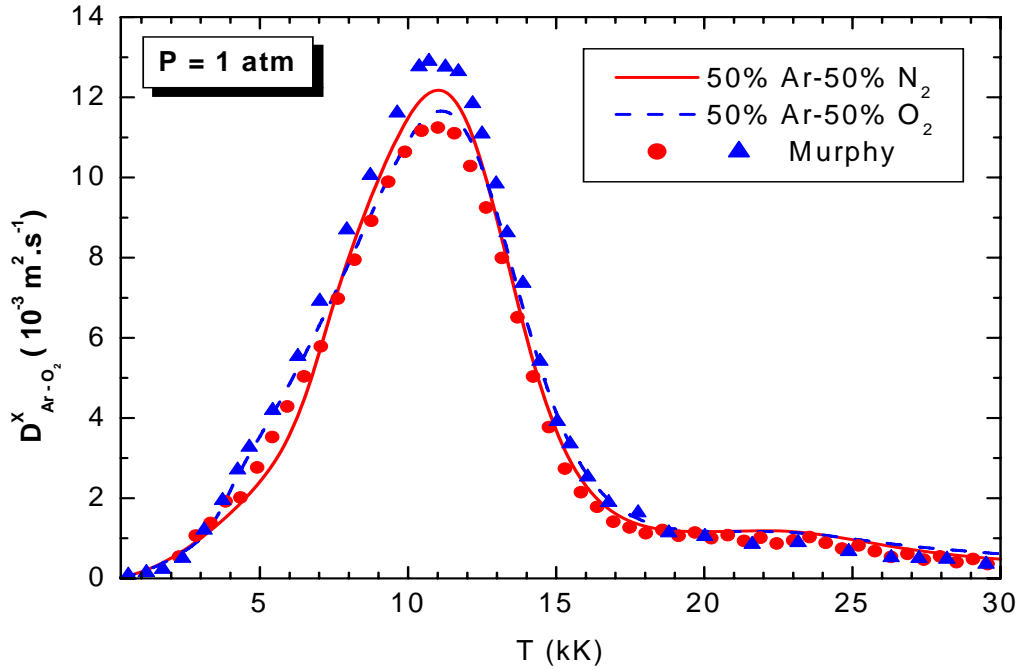


Figure 1. Combined ordinary diffusion coefficient of nitrogen or oxygen in argon at atmospheric pressure (mole proportions).

Concerning the values of the CODC, these last are close to those obtained for the binary diffusion coefficient of Ar-N₂ when the temperature is lower than 5500K whereas the coefficient is similar to the values of the binary coefficient Ar-N for temperatures between 8000 K and 10000 K. Indeed, for these two ranges of temperature, Ar, N₂ and N represent the majority of the species in the thermal plasma. Beyond 10000 K, the CODC decreases because the ionic species become predominant.

In another publication [16] we presented some results for Ar-He mixtures. The agreement with previous results computed by Murphy [17] was good: exactly the same values of amplitude of the combined diffusion coefficients at the peak in the evolution of this coefficient versus temperature, with a slight shift of this peak. Finally, figures 2a and 2b compare our results [16] with those proposed by Murphy [18] and Aubreton *et al* [19,20] in the case of 50%Ar-50%Cu mixture (in molar proportions) and various pressures (0.5atm, 1atm and 2atm). The shape of the CODC is similar and the small discrepancies observed on the amplitude are due to different values of collision integrals. Concerning the influence of the pressure, the increasing of this parameter reduces the amplitude of the peak and moves it towards higher temperatures. More details will be supplied in the following part treating the Air-metals mixture.

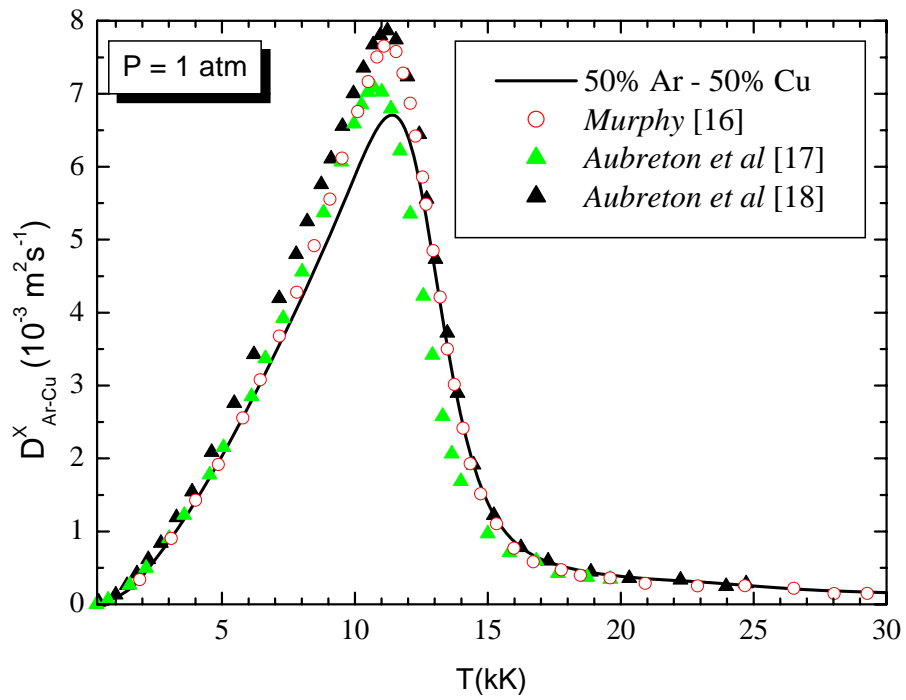


Figure 2a. Combined ordinary diffusion coefficient of copper in argon at atmospheric pressure (mole proportions).

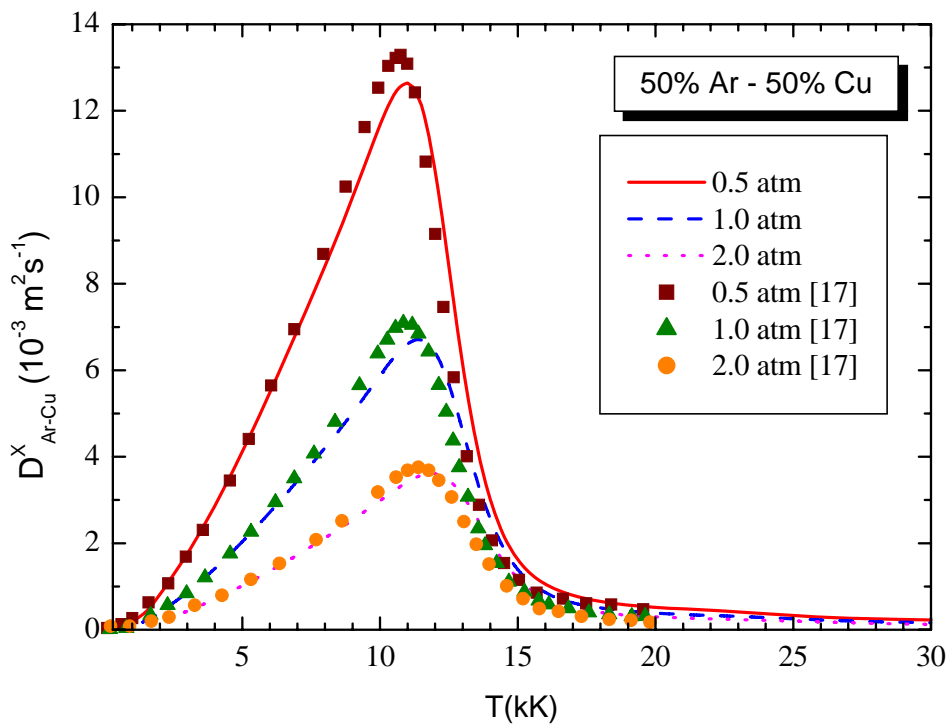


Figure 2b. Combined ordinary diffusion coefficient of copper in argon for different pressures (mole proportions).

4. Results for air-metal mixtures

In this part, we present some results of the combined diffusion coefficients obtained for the three metal vapours (Ag, Cu and Fe) in Air plasmas. These coefficients can be directly used in models to calculate the particle flow or the mass flow of the metal. For those mixtures, the assumptions given by Murphy to use the previous expressions are valid because the metal oxides (FeO, CuO or AgO) exist only at very low temperatures and have almost no impact on the results.

Figures 3 and 4 show the evolution of the CODC as a function of temperature for various concentrations of metal, for both iron and copper metals (for air-metal mixtures the percentages are given using mass proportions). Its general behaviour with temperature is consistent with the results presented in the literature for other mixtures. Indeed, we observe a maximum for temperatures around 10 kK. This maximum depends significantly on the concentration of the metal in the mixture. As mentioned by Murphy in several papers, this dependence is indirect and is due to the influence of gas proportions on the ionisation degree of the plasma. In the low temperature range, the coefficient increases with temperature because of the diffusion between neutral particles (atoms and molecules) whereas the plasma is dominated by Coulombian interactions at high temperature which strongly decreases the electrons and ions mobility and does not favour the diffusion.

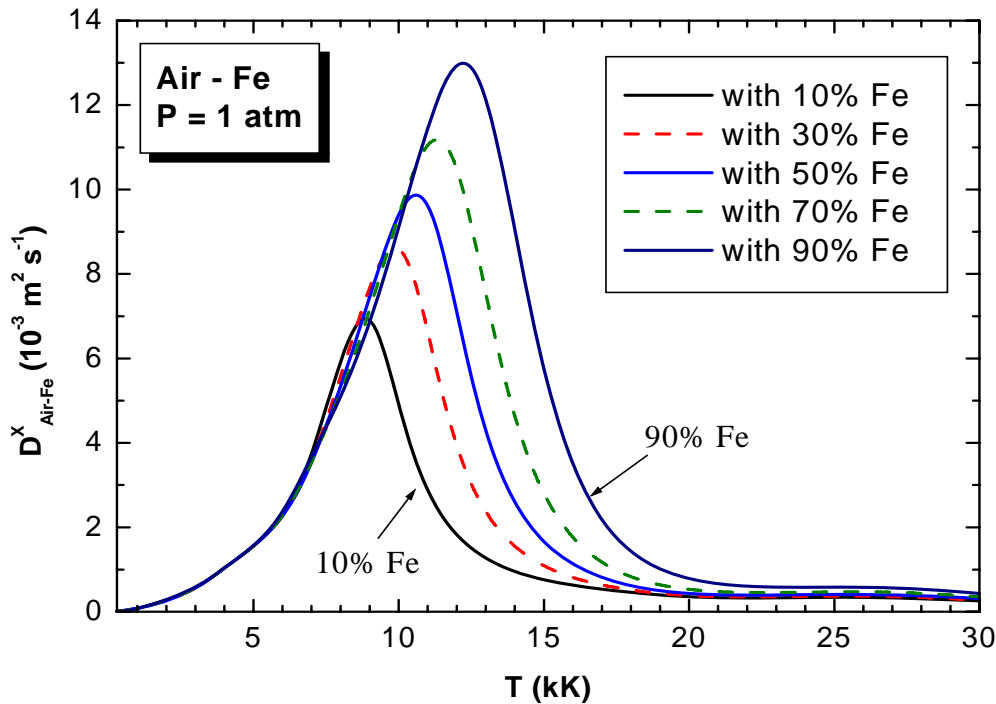


Figure 3. Combined ordinary diffusion coefficient of iron in air at atmospheric pressure, for different concentrations of iron in the mixture (mass proportions).

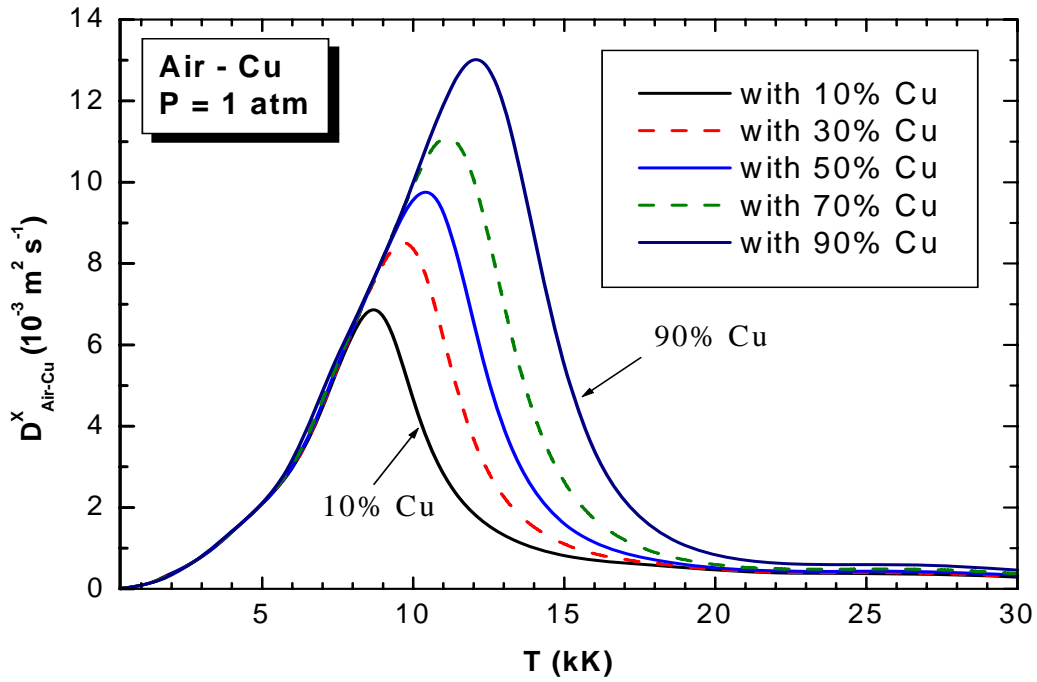


Figure 4. Combined ordinary diffusion coefficient of copper in air, for different proportions of copper in the mixture (mass proportions).

Comparison of figures 3 and 4 shows that the CODC is very similar in air-Fe and air-Cu plasmas, which is confirmed in figure 5 showing the influence of the metal vapour nature on the CODC for the same concentration of vapour in the mixture and the same pressure: 10% mass of metal and atmospheric pressure. We note a very similar behaviour with the temperature of the CODC for the three metals. However, the maximum observed with 10% of silver is lower than the two others and appears at lower temperatures. This behaviour can be explained by the combination of two properties: the atomic masses and the ionization energies of the two gases (Air and vapour). Indeed, this maximum value increases when the gas having the lowest mass is increasingly present in the plasma (107.87g/mol for silver, 63.546g/mol for copper and 55.85g/mol for iron).

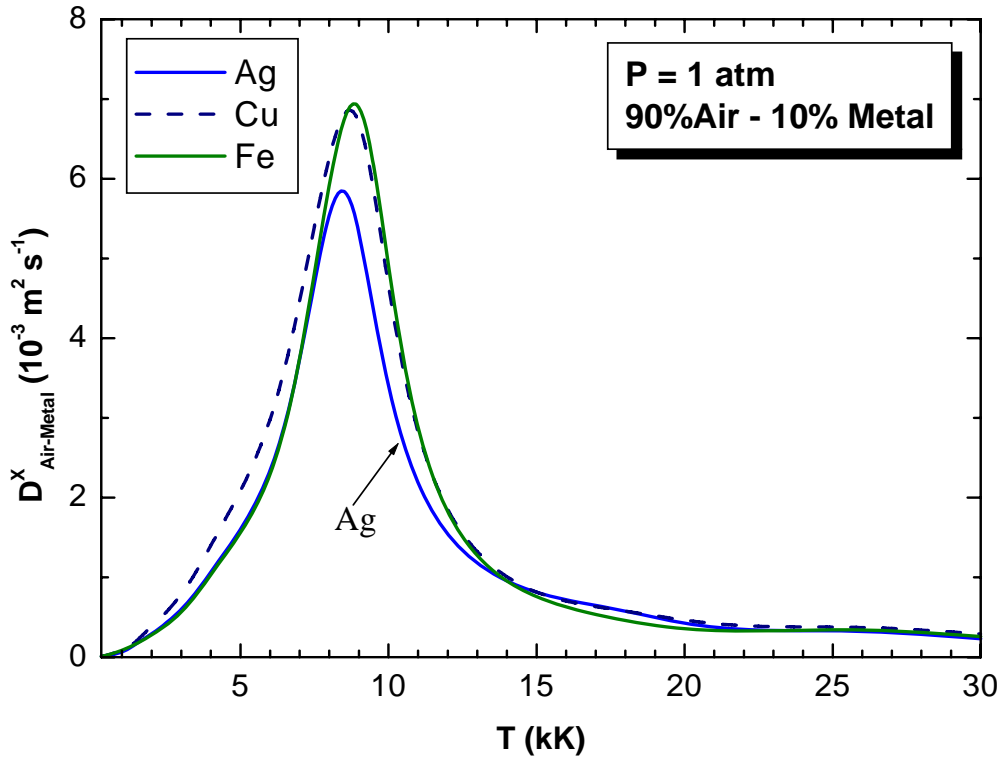


Figure 5. Influence of vapour nature on the combined ordinary diffusion coefficients (mass proportions).

It is also interesting to note that the maximum of the CODC evolution versus temperature moves towards higher temperatures when the concentration of metal vapour increases, as it can be seen in figures 3-4. Our previous works [16] and literature results [17] show that this behaviour is almost general: the peak is shifted to the highest temperatures when the proportion of the gas (or vapour) having the lowest ionisation potential, increases in the mixture (this behaviour is not observed when the ionisation potentials and the masses of the atomic species in the mixture are similar, as for the case of oxygen-nitrogen plasmas [21]; the CODC is then almost independent of the gas proportions).

Figure 6 shows the influence of the pressure on the CODC. Results are given for Air-Cu mixture but behaviours are similar for the other vapours. When the pressure increases, the combined ordinary diffusion coefficient decreases due to a decrease of the mean free path. We also observe that the position of the peak moves towards the higher temperatures in agreement with the mass action law (expressed here with Saha equation): the ionization of the gases is shifted to the high temperature when pressure increases.

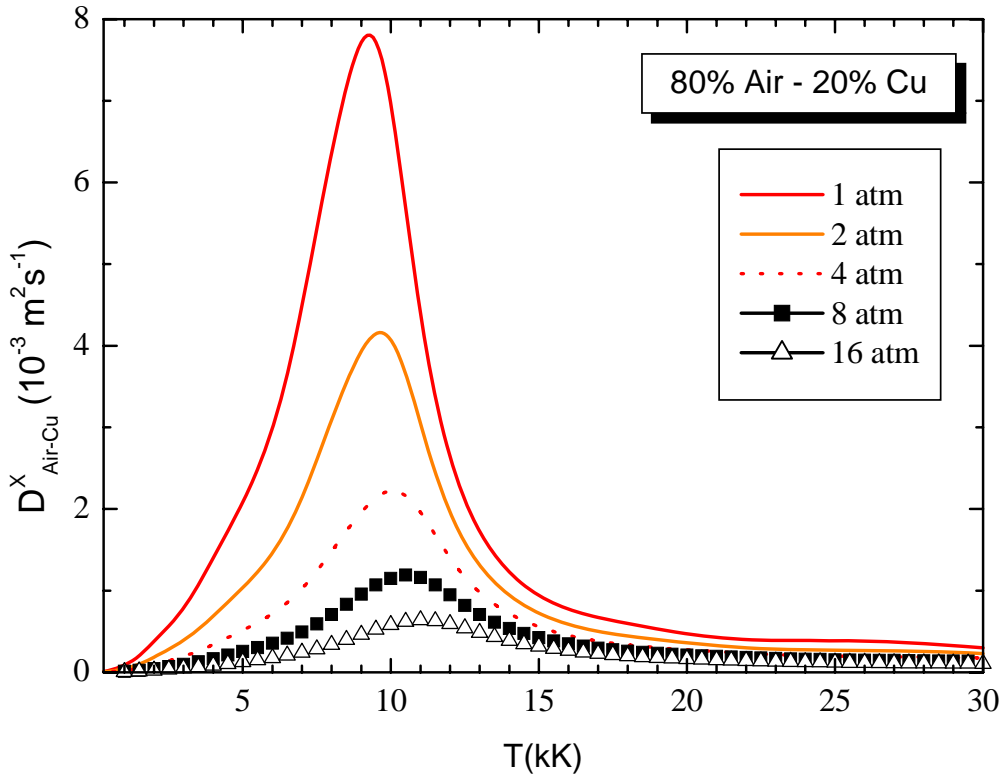


Figure 6. Influence of pressure on the evolutions of the COCD in air-copper mixtures (mass proportions).

Finally, an example of the electric field diffusion coefficients is given on figure 7 for different mixtures. These coefficients describe the diffusion of charged particles due to the applied electric field. They are directly linked to the masses, the ionization energies and the presence of charged particles. The electrical field acts preferentially on the more strongly ionized gas. At low temperatures, $\overline{D_{AB}^E} \cong 0$ because of the very small electron number density. It has to be noted that with this calculation method we obtain the computational equality $\overline{D_{AB}^E} = -\overline{D_{BA}^E}$ as it can be seen on figure 8.

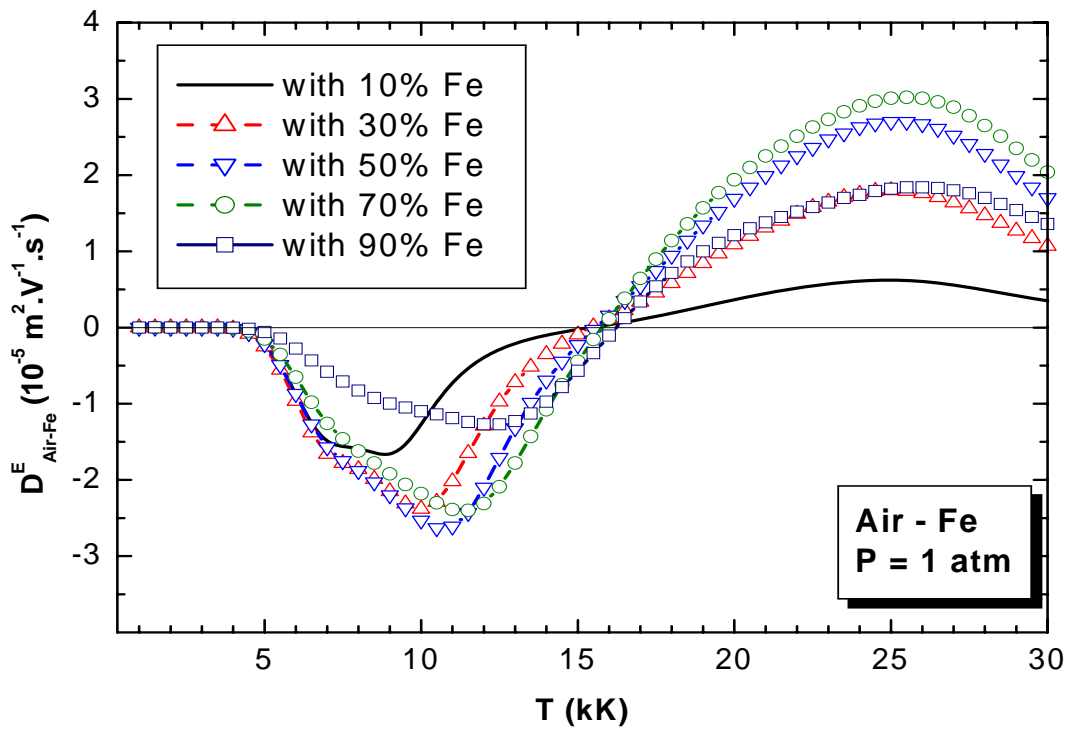


Figure 7. Combined diffusion coefficients due to gradients of electric field, in Air-Fe mixtures (mass proportions).

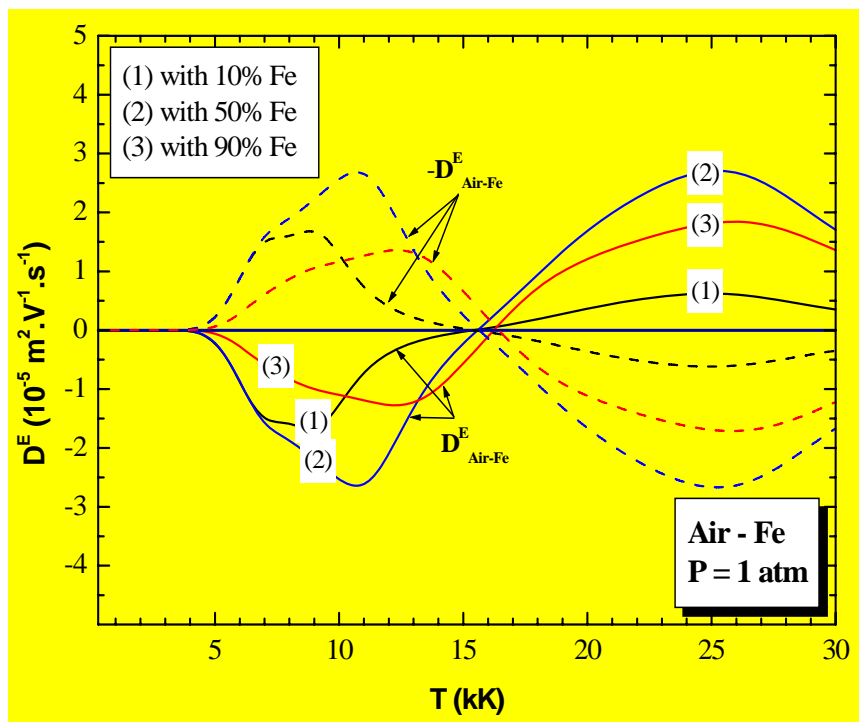


Figure 8. Validity of the condition $\overline{D^E_{AB}} = -\overline{D^E_{BA}}$ for the combined diffusion coefficients due to gradients of electric field, in Air-Fe mixtures (mass proportions).

5. Conclusion

In a previous paper [15] we presented the calculation of equilibrium composition, thermodynamic functions, transport coefficients (viscosity, electrical and thermal conductivities) and radiative properties for air-metal mixtures. We have completed here the material data for these mixtures by calculating the diffusion coefficient, allowing a general modelling of electric arcs in air in presence of metal vapour. Our calculation is based on the method of combined diffusion coefficients proposed and developed by Murphy. In a general point of view the diffusion flux depends on several gradients (particle density or mass proportion, temperature, pressure) and of external forces such as those created by an electric field and thus 4 kinds of combined diffusion coefficient can be introduced. We have mainly limited our contribution to the calculation of the CODC (combined ordinary diffusion coefficient relating the diffusion flux to the gradient of mass proportion) because in the arc model the authors generally limit the role of diffusion to this term, the other diffusion phenomena having a second order influence. It must also be noted that normal diffusion is often a weak phenomenon among those participating to the evolution of plasma composition, in particular convection, turbulent diffusion and chemistry.

After validation of our calculation method using comparison with literature for other mixtures, our results for air-metal mixtures show that the nature of metal among copper, iron and silver is rather weak. The results for copper and iron are almost identical because the atomic mass and the ionisation potential are very similar, whereas the diffusion coefficient with silver is slightly lower because of the highest atomic mass of this metal. We have also explained that the evolution of the CODC with the metal proportion is due to the relative ionisation of the metal: the diffusion coefficient peak is shifted to the highest temperatures when the metal proportion increases. Finally the diffusion coefficient decreases when pressure increases which was a foreseeable result.

Acknowledgments

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