

BASIC DATA: COMPOSITION, THERMODYNAMIC PROPERTIES AND TRANSPORT COEFFICIENTS APPLIED TO FUSES.

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Abstract: Two main areas of research can be determined for the basic data that are composition, thermodynamic properties and transport coefficients: the polyphasic area and the gas phase and plasma phase area. In the case of mixture of (Ag, SiO₂) that can be found in fuses field, we depict the main results available at the present time.

Keywords: e.g. fuse, composition, transport coefficients, polyphasic, thermal plasma.

1. Introduction

Two main areas of research can be determined for the basic data: the polyphasic area and the gas phase and plasma phase area. In the case of mixture as Ag-SiO₂, few studies are given [1-4]. The fuse operation can be described by successive steps [5, 6]: firstly the electric current produces the heating of the silver strip around constrictions; secondly, the fusion and the vaporization of the constriction opens a gap in which an electrical arc is initiated; thirdly, the arc interacts with the surrounding silica sand and the silver fuse element continues to melt and to vaporize (burn-back) [7, 8] until the circuit voltage is not high enough to maintain the arc.

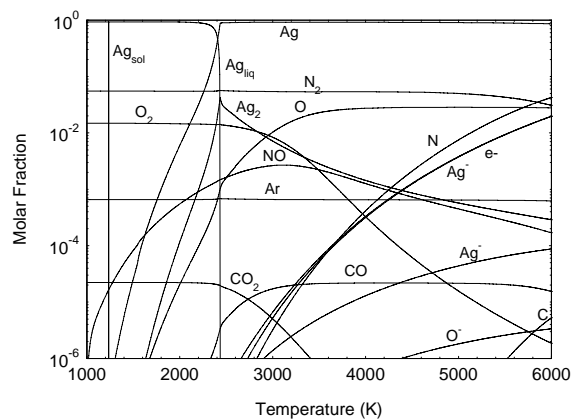
In this paper we give some results for the polyphasic area: composition, enthalpy and pressure dependence on temperature and for the gas and plasma phase we give the composition, the enthalpy, the viscosity, the electrical and thermal conductivities.

2. Polyphasic area

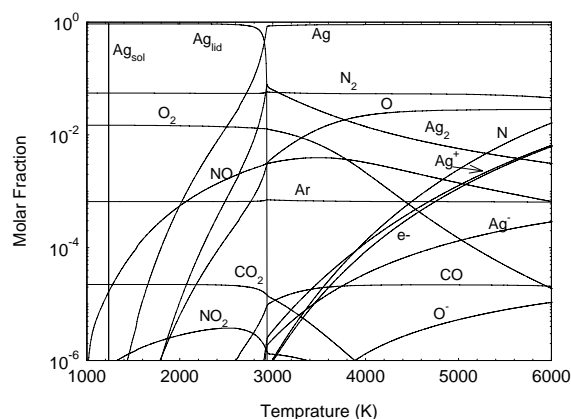
By using a Gibbs Free Energy minimization method [3, 9], one can obtain the molar fraction versus temperature. Firstly since the silver ribbon melt and vaporized, one can assume that the mixture is mainly composed of silver and air. Furthermore the temperature increases due to Joule heating the pressure increases. That is why the calculation has been made with air and silver for two pressures: 1 bar and 10 bars. For these calculation we take into account : 16 monatomic species Ar, Ar⁺, Ag⁻, Ag, Ag⁺, C, C⁻, C⁺, O, O⁻, O⁺, N, N⁺, Si, Si⁺, Si⁻ and

electrons, 23 diatomic species Ag₂, C₂, C₂⁻, C₂⁺, CN, CN⁻, CN⁺, CO, CO⁻, CO⁺, CSi, N₂, N₂⁻, N₂⁺, NO, NO⁻, NO⁺, NSi, O₂, O₂⁻, O₂⁺, Si₂, SiO and 15 polyatomic species CNO, CNN, CO₂, CO₂⁻, NO₂, NO₃, N₂O, NCN, NO₂⁻, NSi₂, N₂O⁺, N₃, O₃, SiO₂, Si₃.

The results of the molar fractions are shown in figures 1 and 2.

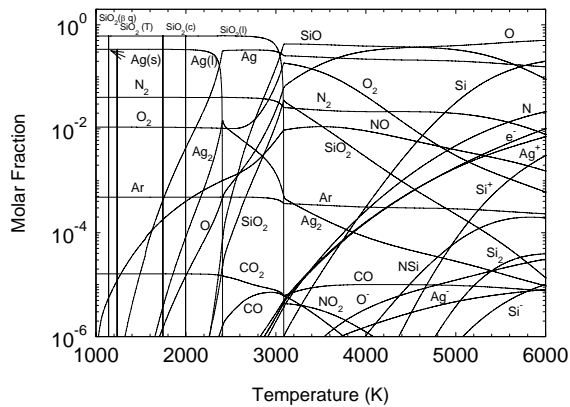


a) P=1 bar

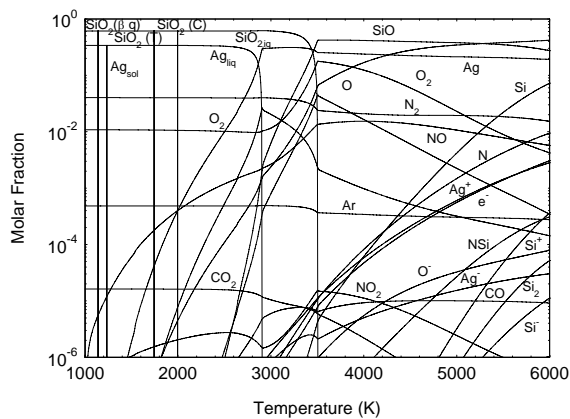


b) P=10 bars

Fig. 1: Molar fractions of chemical species versus temperature calculated at 1 bar and 10 bars. The weight percentage of air is fixed at 2% and for the silver at 98%.



a) P=1 bar



b) P=10 bars

Fig. 2: Molar fractions of chemical species versus temperature calculated at 1 bar and 10 bars. The weight percentage of air is fixed at 2% and for the silver at 49% and for SiO₂ at 49%.

Figure 1 shows the molar fraction for silver and air: 98% Ag and 2% of Air in weight percentage for two pressures 1 and 10 bars. Figure 2 shows the molar fraction for mixture of silver, silica and air: 49% SiO₂, 49% Ag and 2% of Air in weight percentage for two pressures 1 and 10 bars.

At low temperature (<1,500 K) the gaseous species are only due to air namely N₂, O₂, Ar and CO₂. The liquid silver vaporizes in gaseous silver Ag for both cases (Fig. 1 and 2). The liquid silica vaporizes in SiO and O₂ (Fig. 2). An increase of NO molar fraction when the liquid silica vaporizes can be observed. So, a part of N₂ reacts with O₂ to produce NO during this vaporization. A break in CO₂ molar fraction can be observed when the liquid silica vaporized. So, the liquid silica vaporization influences the dissociation of CO₂. The monatomic species Si is mainly due to the dissociation of SiO at high temperature (>5,000 K) and the dissociation of SiO₂ and SiO for lower temperature. The electrical neutrality between charged particles is mainly made between Ag⁺ and electrons.

The vaporization of silver and SiO₂ appears for higher temperature when the pressure is higher (Fig. 1 and 2). At low temperature, the gaseous species are those of air. The liquid silver vaporizes at 2,400 K for 1 bar and 2,915 K for 10 bars in the case of considered mixture of SiO₂, Ag and Air. The liquid silica vaporizes in SiO and O₂ for temperatures around 3,090 K at 1 bar and 3,500 K for 10 bars. Then O₂ dissociates in O, SiO dissociates to give Si and O. These latter become the main chemical species. The polyatomic species are still observed present at higher temperatures for higher pressures, for example, CO₂. Molar fraction of NO₂ has a higher value for 10 bars than for 1 bar. Since the ionization appears at higher temperature, the electronic concentration is lower for higher pressures. The electrical neutrality is made mainly between Ag⁺ and e⁻ for lower considered pressures and between Ag⁺, e⁻, O⁻ and Ag⁻ for higher pressures.

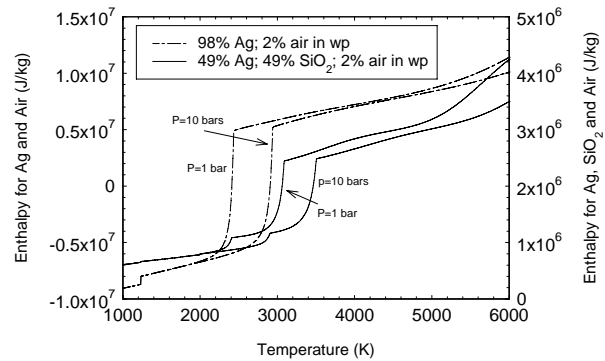


Fig. 3: Enthalpy versus temperature calculated at 1 and 10 bars for mixtures of air with silver and air with silica and silver.

Figure 3 shows the calculated total enthalpy versus the temperature for silver with air and silica and silver with air at 1 bar and 10 bars. Concerning the silver with air, two breaks in the enthalpy curves can be observed. The first break corresponds to the melting of solid silver at a temperature of 1,234 K and the second break to the vaporization of liquid silver at a temperature around 2,400 K for a pressure of 1 bar and 2,900 K for a pressure of 10 bars. Concerning the silica and silver with air, a break around a temperature of 3,050 K for 1 bar and 3,450 K for 10 bars that corresponds to the silica vaporization can be observed. The two breaks associate to silver vaporization can also be noted. The phase changes of silica, namely, β -quartz to tridymite, tridymite to cristobalite and cristobalite to liquid silica and the phase change of silver liquid to solid can be hardly seen due to the enthalpy scale. As a matter of fact, the involved energies in this phase transformations are low [9].

The vapor pressure of Ag can be deduced from the partial pressure of gaseous Ag. By using an

equation as $\text{Log}(p_{\text{vap}}) = A + B/T + C \text{Log}(T)$ with p_{vap} in mm of Hg and T in K, the vapor pressure of Ag is well approximated with $A=11.3$, $B=-14,300$ and $C=-0.738$. Concerning the vapor pressure of SiO_2 , since liquid SiO_2 vaporizes mainly in SiO and O_2 . These two molecules reacting with the air, the vapor pressure can not be directly deduced from the partial pressures. Nevertheless, with a calculation pressure dependence on temperature in SiO_2 , the coefficients can be determined. So the vapor pressure of SiO_2 is well approximated with $A=26$, $B=-31,600$ and $C=-3.76$. So we have to calculate the temperature dependence on pressure for each mixture of silica, silver and air.

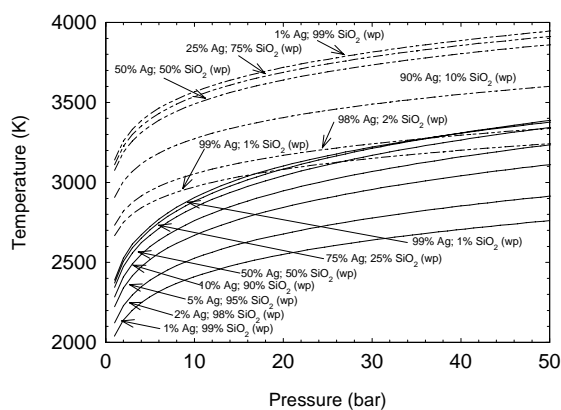


Fig. 4: Vaporization temperature of liquid silver and liquid silica calculated for various pressures. The weight percentage of air is fixed at 2% and the silver and silica proportion is given in weight percentage.

In figure 4, the vaporization temperatures of liquid silver and liquid silica calculated for various pressures are given. A large variation of vaporization temperature around a factor 1.3 between silver percentages of 1% to 75 % for a given pressure can be observed; for higher silver percentage the variation in vaporization temperature is lower. For vaporization temperature of liquid silica, a large variation around a factor 1.2 between silica weight percentages of 1% to 50 % for a given pressure can be observed; for higher silica percentage the variation in vaporization temperature is lower.

3. Gas and plasma phase

The transport coefficients and the thermodynamic properties, in the field of high temperatures ($> 4,000$ K) and high pressures (1 to 30 atm.), are essential data in the modelling of plasma processes during the fuse operation [11]. To determine the transport coefficients, we use the well-known solution of the Boltzmann equation due to Chapman and Enskog

[12, 13]. This assumes two-body interactions between chemical species. This interaction can be described by a potential interaction between two particles. By successive integrations of these potentials, we obtain collision integrals which are the basic data of the transport coefficients. The potentials depend on the type of molecules that interact [14]:

- Neutral-neutral molecules
- Charged-neutral molecules
- Charged-charged molecules
- Electron-neutral molecules

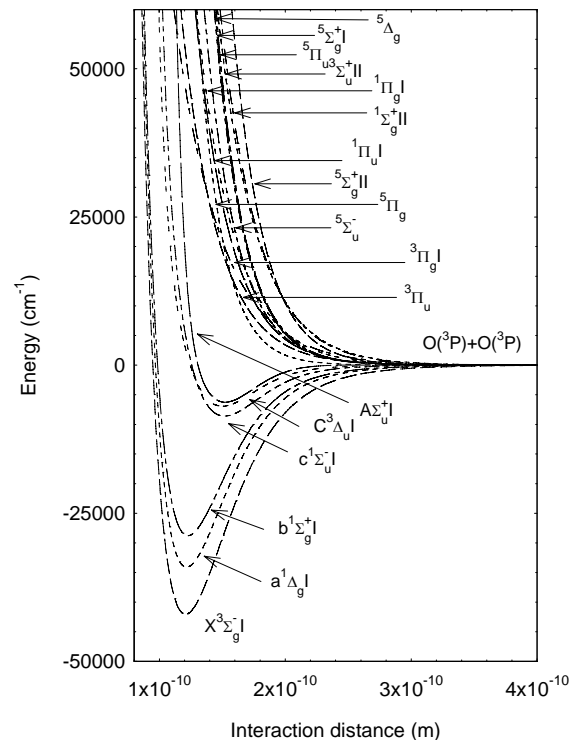
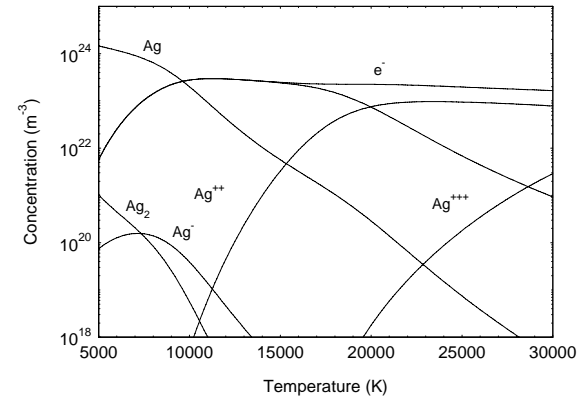


Fig. 5: Hulbert-Hirschfelder and repulsive potentials taken into account for the interaction between oxygen atoms versus the interaction distance.

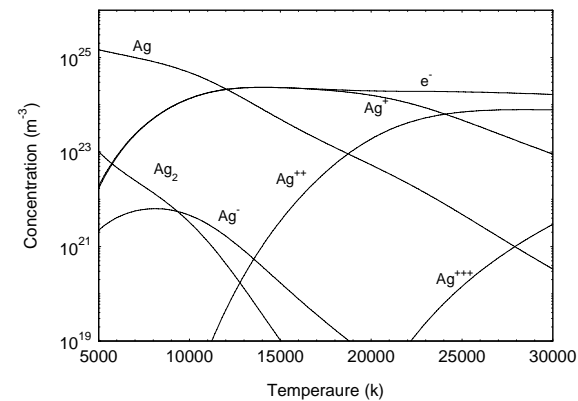
In figure 5, the potential curves are represented in the case of (O, O) in ^3P state. For the two other collisions (Ag, Ag) and (Si, Si) the results are given in [4]. From these three collisions one can obtain a Lennard Jones potential [12] that allows to obtain all the potential for the collisions between neutral molecules with the help of combination rules.

For the collisions between neutral and charged molecules a non elastic process namely charged transfer has to be taken into account. For the elastic processes we consider a dipole potential. For the collision between the charged molecules we consider a Coulomb potential shielded by a Debye length. For collisions between electron and neutral species, the collision Integrals are obtained from the literature or from the polarisability of neutral species.

Thus the data base to obtain all the collisions integral from the potential are determined. We have to calculate the composition for high temperature. From a Gibbs energy method [1, 3], we obtain the composition versus temperature. We have chosen to study two plasmas: silica plasma and silver plasma.

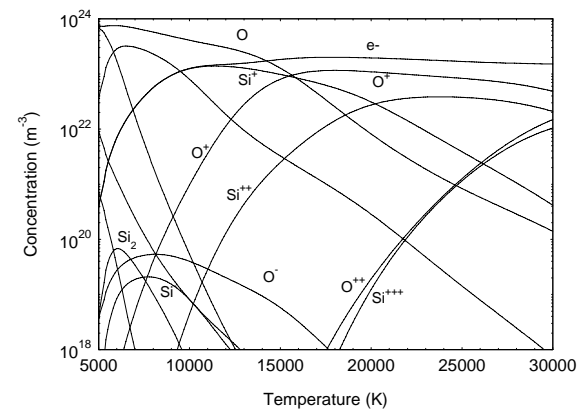


a) P=1 atm

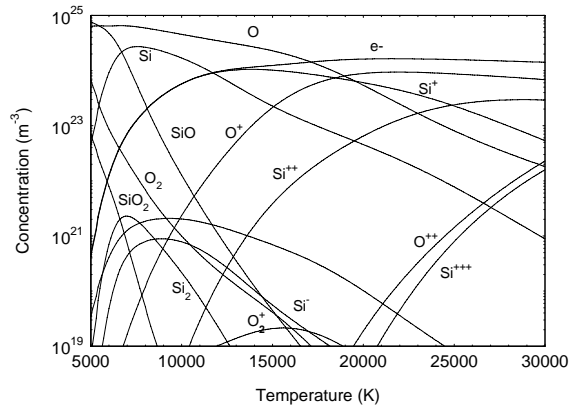


b) P=10 atm

Fig. 6: Composition calculation of silver plasma versus temperature for two pressures



a) P=1 atm



b) P=10 atm

Fig. 7: Composition calculation of silica plasma versus temperature for two pressures.

We give the concentration versus the temperature for silver plasma in figure 6. The main species in temperature range from 5,000K to 9,550K at 1 atm and in temperatures range from 5,000K to 12,000K is monatomic silver. For high temperature the main chemical species is electrons. The electrical neutrality is made between electrons and ionized silver before 19,900 K for 1 atm and 24,000 K for 10 atm and then with silver ionized two times for higher temperature.

For silica plasma the concentration is given in figure 7. The main species is monatomic oxygen between 5,000 K and 14,000 K for 1 atm and between 5,000 K and 17,000 K for 10 atm. For higher temperature the main chemical species is electrons.

By comparison the graphs devoted to 1 atm and those devoted to 10 atm, we remark that the ionisation of neutral species appears at higher temperature for higher pressure.

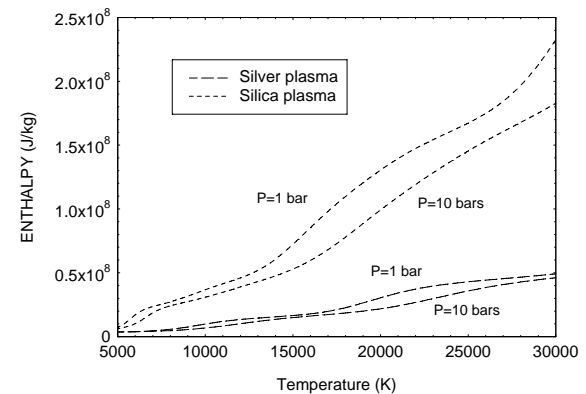


Fig. 8: Massic enthalpy versus temperature for silica plasma and silver plasma for two pressures.

Once the concentration calculation is made we can determine the enthalpy versus temperature. We present the results in figure 8. As we remark previously higher pressure higher temperature for which the chemical reaction appears. So for a given enthalpy the temperature is higher for a higher

pressure. Some changes in the slope of the curve can be associated to chemical reactions. In the case of silica plasma around 5,200 K the dissociation of SiO appears and around 14,000 K for 1 atm and 17,000K for 10 atm appear the ionisation of oxygen. In the case of silver plasma, the change of the slope around 9,550K at 1 atm and 12,000K at 10 atm can be associated to the ionisation of monatomic silver.

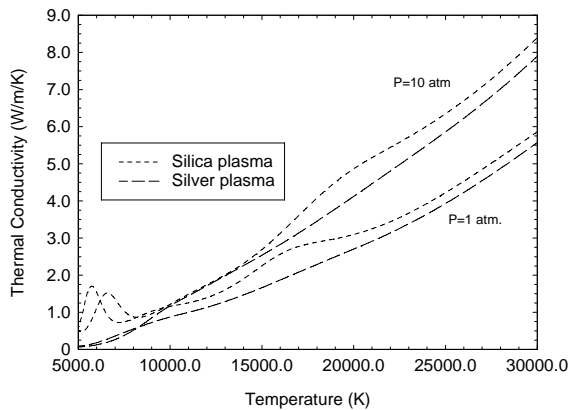


Fig. 9: Thermal conductivity versus temperature for silica plasma and silver plasma for two pressures.

In figure 9, we plot the thermal conductivity for the two considered pressures and for the two considered plasmas. The total thermal conductivity λ_{tot} can be separated into four terms with a good accuracy [15, 16]:

$$\lambda_{tot} = \lambda_{tr}^e + \lambda_{tr}^h + \lambda_{int} + \lambda_{react}$$

where λ_{tr}^e is the translational thermal conductivity due to the electrons, λ_{tr}^h the translational thermal conductivity due to the heavy species particles, λ_{int} the internal thermal conductivity and λ_{react} the chemical reaction thermal conductivity. The peak appearing in the thermal conductivity can be associated to the chemical reactions. Since the chemical reaction is made at higher temperature for higher pressure, the peak associated to SiO dissociation appears at higher temperature: 5,700K at 1 atm., 6,600 K at 10 atm. When the electrons become the main species the thermal conductivity due to the electron become the main contribution to the total thermal conductivity. Since the electronical thermal conductivity follows the electrons density and that electrons density follows the Dalton law, we observe higher thermal conductivity for higher pressure.

In figure 10, we plot the viscosity versus temperature for the two considered pressures and for the two considered plasmas. For silver plasma the results show an increase followed by a decrease versus temperature. Since the degree of ionization depends on the pressure, the temperature at which the peak occurs depends on the pressure. We obtain 6,300 K

for 1 atm., 7,750 K for 10 atm for silver plasma. In the case of silica plasma, we obtain two peaks at 7,500 K and 11,750 K for 1 atm, 8,800K and 13,600K for 10 atm. The first change in the slope is mainly due to the dissociation of SiO; the second peak is due to the ionisation of O.

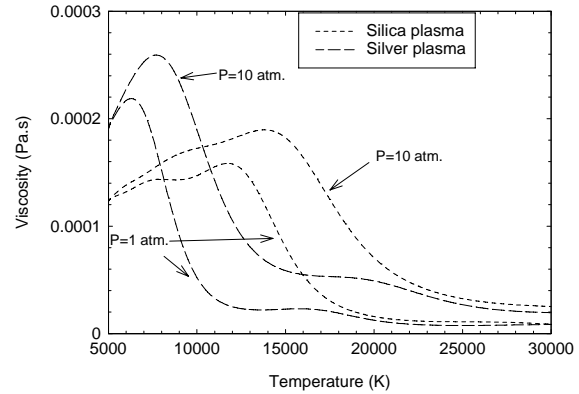


Fig. 10: Viscosity versus temperature for silica plasma and silver plasma for two pressures.

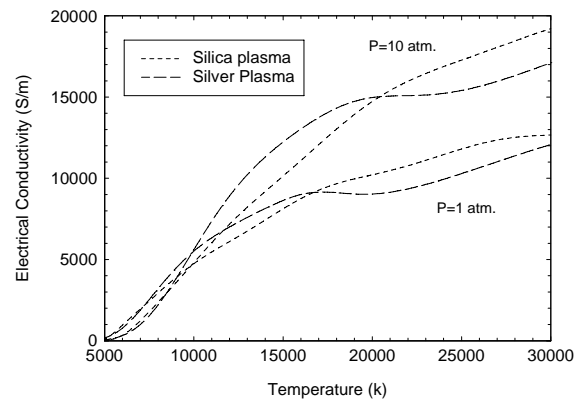


Fig. 11: Electrical conductivity versus temperature for silica plasma and silver plasma for two pressures.

In figure 11, we present the influence of pressure on the electrical conductivity for the two considered plasmas. For the same pressure, the electrical conductivities differ for the two plasmas. The reason is that the electrical neutrality is not made between the same species, that is to say between e^- , Ag^+ and Ag^{++} for silver plasma and between e^- , Si^+ , O^+ and Si^{++} . When pressure is higher, the ionization appears at higher temperatures. So, the electron density is lower at low temperatures. Consequently, the electrical conductivity is lower. When the pressure is higher and when the plasma is fully ionized, the electrons density follows the Dalton law and its value is higher. So, we observe higher electrical conductivity.

4. Conclusion

From the calculation of the composition in the polyphasic area we have shown the great role played by the chemical species. Notably with the liquid silica that are transformed in monoxide silica and oxygene. This temperature of vaporization depends on the proportion of silver with silica. The electrical neutrality is mainly made between ionized gaseous silver and electrons even with a low amount of silver. So, at low temperature the electrical conductivity depends on silver. When the pressure and the amount of silver are high, there is an increase in molar fraction of electronegative chemical species as Ag⁺ and O⁻.

In the gas and plasma phase, we have compared and explained the results of transport coefficients for two plasmas: silica plasma and silver plasma at 1 atm and 10 atm. The remarkable results are concerning the viscosity. The silver plasma has a lower viscosity between 10,000 K and 20,000 K at atmospheric pressure 15,000 K and 25,000 K for 10 atm. and between 17,000 K and 27,000 K for 30 atm. than the silica plasma This result explains the fact that we observe silver at a large distance from the fuse element and also can explain the variation of the composition in the fulgurite after the working of the fuse. Furthermore we have presented all the data needed to model the fuse working: electrical and thermal conductivity, enthalpy, viscosity.

The development of such calculation will be made with the kinetics chemical reactions to involve time scale lower than 1 ms and by the addition of compounds as CaF₂.

Acknowledgments

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