

Water Vapor Influence on Thermodynamic Properties of Air-water Vapor Mixtures Plasmas at Low Temperatures

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Abstract The thermodynamic properties of plasmas formed by air and water vapor mixtures is calculated in the temperature range from 500 to 12 000 K at atmospheric pressure and local thermodynamic equilibrium (LTE). The Gibbs free energy minimization method is used to determine the equilibrium composition of the plasmas which is necessary to calculate the thermodynamic properties. Then the thermodynamic properties are also used to calculate the density of energy and the power flow of plasmas concerned. The results are presented and discussed according to the rate of water vapor. The results of the density of energy and power flow show in particular that the increasing of the rate of water vapor in air can be interesting for power cut. This could improve the performance of plasma during current breaking in air.

Keywords: equilibrium composition, Gibbs free energy, plasma, thermodynamic properties

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1. Introduction

The electrical current breaking is often obtained by separating electrodes in air or in compressed air [1,2]. If a short-circuit appears in the electrical circuit, the contacts of the circuit breaker apparatus are separated and create an electric arc [1,2,3]. This arc interacts with environment gas and generates a plasma of this gas [1,2]. Several studies on the electrical arc have shown the influence of the insulator vapor [1,5,6,7,8,9], metal of electrodes contacts [1,10,11,12,13] and hydrogen atoms [1,2,5,8] on the plasmas characteristics during the breaking. In this study, we are interested by the influence of water vapor on plasma characteristics during electrical current breaking. The knowledge of thermodynamic properties is fundamental to evaluate and compare the performance of plasmas in current breaking [5]. The purpose of this paper is to calculate the thermodynamic properties versus temperature of thermal plasmas formed by air-water vapor mixtures. This mixture can be naturally formed because water vapor is present in atmospheric air [1,2]. But the rate of water vapor in the atmospheric air is inferior to 7% at temperature of 40°C [1,2]. We choose to study air-water vapor mixtures with often high water vapor percentage. The concerned plasmas are: 95% air - 5% water vapor; 90% air - 10% water vapor; 50% air - 50% water vapor;

20% air - 80% water vapor. The proportion of air and water vapor of chosen mixture are given in volume. These four (4) mixtures are chosen to be able to determine the water vapor influence on the plasmas thermodynamic properties. The high proportion of water vapor in the mixture could be done during the current breaking by water injection. Supposing local thermodynamic equilibrium (LTE), calculations are made in a temperature range from 500 K to 12000 K at pressure of 1 atm. We suppose that the air is constituted by 80% of nitrogen (N_2) and 20% of oxygen (O_2). In the [Figure 2](#), we compare our results of dry air plasma with those of P. Fauchais and al. at atmospheric pressure and in the temperature range from 500 K to 12000 K. Then, we present and discuss our results of mass density, specific enthalpy, specific heat capacity, density of energy and power flow of plasma formed of air-water vapor mixture plasma.

2. Calculation of Thermodynamic Properties

The initial step in the calculation of thermodynamic properties is the determination of the equilibrium composition of the gas with chemical equilibrium. Two main methods are generally used for the determination of the equilibrium composition of the plasma: the method based on the law of mass action using the laws of Saha

and Guldberg-Waage [2,14,15,17] and that based on the minimization of the Gibbs free energy using Lagrange multipliers [19-26]. In this work we have used the minimization of the Gibbs free energy. Neutral and charged species are considered. For air-water vapor mixture, we take into account 11 monatomic species: H, H⁻, H⁺, N, N⁻, N⁺, N⁺⁺, O, O⁻, O⁺, O⁺⁺, and electrons; 18 diatomic species: H₂, H₂⁻, H₂⁺, N₂, N₂⁻, N₂⁺, NH, NH⁻, NH⁺, NO, NO⁻, NO⁺, O₂, O₂⁻, O₂⁺, OH, OH⁻, OH⁺, and 11 polyatomic species: O₃, H₂O, N₂O, NH₃, N₂O₃, HNO₂, HO₂, N₂O₄, H₂N₂, N₂O₅, HNO₃. The monatomic and diatomic specific thermodynamic properties as enthalpies, chemical potentials are calculated by the fitting coefficients in refs. [27]. For polyatomic chemical species their specific thermodynamic properties are obtained in Janaf tables [28].

The electro-neutrality is automatically verified by the calculation [29]. We suppose local thermodynamic equilibrium (LTE). In Figure 1, we give the composition of plasma formed of 95% air - 5 % water vapor. In this figure, we represent the concentration of chemical species versus temperature at atmospheric pressure and local thermodynamic equilibrium (LTE). We can see three (3) phases. The first phase concerns temperature less than 1500 K (T < 1500 K). In this domain, the main chemical species are: N₂, O₂ and H₂O. The second phase concerns the temperature range of 1500 K to 6000 K (1500 K < T < 6000 K). In this interval, the main chemical species are: N₂, O₂, H₂O, NO, OH, H₂, N, O and H. The third phase concerns temperature above 6000 K (T > 6000 K). In this range, the main chemical species are: N, O, H, H⁺, O⁺, N⁺ and e⁻. In low temperatures (T < 5000 K) the electrical neutrality is made mainly between e⁻ and NO⁺ because the ionization energy of the particle NO is low. For high temperatures (T > 5000 K), the ionization of the atoms H, O and N take place in the production of electrons and electrical neutrality is made mainly between e⁻ and N⁺, O⁺, H⁺.

The water molecule H₂O dissociates in OH and H around 3000 K. O₂, H₂ and OH molecules dissociate around 3500 K. The particle NO dissociates in N and O around 5000 K. Nitrogen molecule N₂ dissociates in N around 7500 K. We note that the polyatomic species: O₃, H₂O, N₂O, NH₃, N₂O₃, HNO₂, HO₂, N₂O₄, H₂N₂, N₂O₅ and HNO₃ appear only in very low temperature and their concentrations are often very low. These particles disappear rapidly with temperature because their dissociation energies are low.

The electronegative chemical species namely: H⁻, O⁻, OH⁻, NO⁻, O₂⁻, N₂⁻ and H₂⁻ species appear with low concentration.

2.1. Density (ρ)

The mass density of the plasma is given by the following formula:

$$\rho = \sum_{i=1}^N n_i m_i \quad (1)$$

Where n_i and m_i are respectively the concentration and the mass of i_{th} chemical species. N is the total number of chemical species in the plasma.

2.2. Specific Enthalpy (H)

The specific enthalpy is calculated by:

$$H = \frac{\sum_{i=1}^N n_i h_i^0}{\sum_{i=1}^N n_i m_i} \quad (2)$$

Where h_i^0 is the molar enthalpy and m_i is the mass of i_{th} chemical species and N is the total number of chemical species. The molar enthalpy of monatomic and diatomic chemical species is calculated by using the fitting coefficients in refs [27]. For polyatomic chemical species their molar enthalpy are obtained in Janaf tables [28].

2.3. Specific Heat Capacity (C_p)

The specific heat capacity at constant pressure can be obtained by the numerical derivation of the specific enthalpy [4,5,21,27,30,32]:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P \quad (3)$$

In practice an approximation to estimate the specific heat capacity is used [5,30,31,32]:

$$C_p = \frac{H(T + \Delta T) - H(T)}{\Delta T} \quad (4)$$

In our calculation we are used $\Delta T = 100$.

2.4. Sound Velocity (α)

The sound velocity is calculated by [5,32]:

$$\alpha = \sqrt{\gamma \frac{P}{\rho}} \quad (5)$$

With $\gamma = \frac{C_p}{C_v}$, P is the pressure and ρ is the density of plasma.

2.5. Density of Energy (D_e)

The knowledge of mass density and specific enthalpy enables to calculate the density of energy by [5,32]:

$$D_e = \rho \cdot H \quad (6)$$

2.6. Power Flow (Φ)

The knowledge of mass density, specific enthalpy and sound velocity enables to calculate the power flow by [5,32,33,34]:

$$\Phi = \rho \cdot H \cdot \alpha \quad (7)$$

3. Results and Discussion

For simplification of writing, in the following, we use the notation given in Table 1 for plasmas concerned.

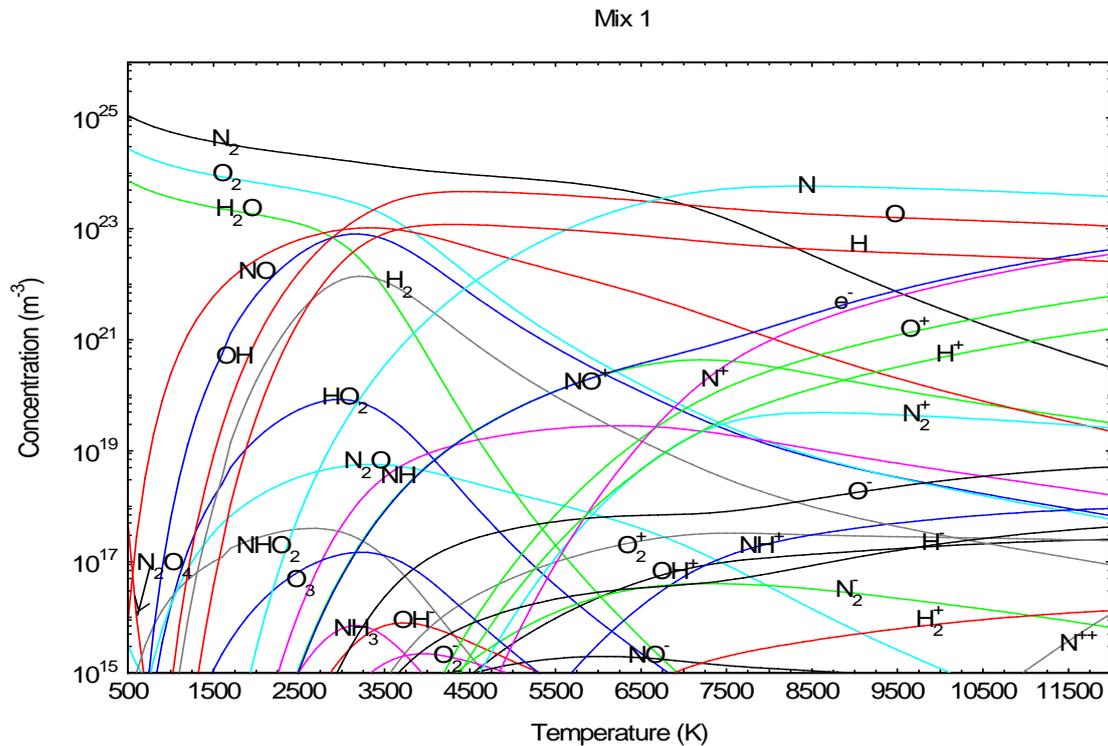


Figure 1. Concentration of chemical species versus temperature at atmospheric pressure and local thermodynamic equilibrium

Table 1. Plasmas studied

Plasma name	Notation
Plasma of 95% air - 5% water vapor	Mix1
Plasma of 90% air - 10% water vapor	Mix2
Plasma of 50% air - 50% water vapor	Mix3
Plasma of 20% air - 80% water vapor	Mix4

3.1. Test of the Calculation Program

To test our calculation code, we compare our results of dry air plasma with those well know of P. Fauchais and al. [35] in the Figure 2. Our values and those of this author are in good agreement. The discrepancy which appears at high temperature on specific enthalpy and specific heat capacity are probably due to the data used in the calculations. We used the method of minimization of the Gibbs free energy and this author has used the law of mass action to determine the equilibrium composition. Also this author does not take the same chemical species into account, especially the polyatomic species.

3.2. Results and Discussion

In the Figure 3, we represent respectively versus temperature, (a) mass density, (b) specific enthalpy, (c) specific heat capacity, (d) sound velocity, (e) density of energy and (f) power flow for various mixtures (Mix1, Mix2, Mix3 and Mix4). The mass density decreases with temperature. It is firstly due to the effect of Dalton's law (at fixed pressure the total number of concentration of particles decreases in respect to $\frac{1}{T}$) and secondly due to the dissociation and ionization reactions which changes

progressively the molecules to lighters atoms, ions and electrons. The mass density decrease, when the rate of water vapor increase in the mixture because the molar mass of water molecule (H_2O) is inferior to that of nitrogen molecule (N_2). The specific enthalpy increases with temperature because dissociation and ionization reactions appear when the temperature increases in the medium. Consequently the energy contained in the plasma increases as temperature rises. The specific enthalpy evolves in the opposite direction of the mass density. The energy necessary of ionization or dissociation produces an abrupt variation of the specific enthalpy. The first abrupt variation around 3000 K corresponds to the dissociation of H_2O and O_2 . The second abrupt variation of the specific enthalpy appearing around the temperature of 7500 K corresponds to the dissociation of N_2 . It is clearly visible for Mix1 and Mix2, but cannot easily be observed for Mix3 and Mix4 because the density of N_2 is high in Mix1 and Mix2 than in Mix3 and Mix4. For temperature less than 3000 K ($T < 3000$ K), the specific enthalpy decreases when the rate of water vapor increases in the mixture.

For high proportion of water vapor in the plasma, specific enthalpy values become negative values in this range of temperature ($T < 3000$ K), due to the negative enthalpy formation of water vapor. For temperatures above 3000 K ($T > 3000$ K) specific enthalpy increases, when the rate of water vapor increases in the mixture. We can say that the presence of free hydrogen atoms (H) in the plasma contributes to increase the specific enthalpy for higher temperatures.

The specific heat capacity at constant pressure is the sum of two terms [5,27]:

$$C_p = C_p^R + C_p^F$$
; The C_p^R is due to the variation of chemical species concentration and the other C_p^F is due

of the variation of the specific enthalpy of each chemical species. The peaks observed on the specific heat capacity curve can be associated with the chemical reactions. The first peak around 3500 K is mainly due to the dissociation of molecules O_2 and H_2O . The second peak around 7500 K is due to the dissociation of molecule N_2 only. If the rate of water vapor increases in the mixture, the intensity of the peak around 3500 K increases and those around 7500 K decreases, because the increasing of water vapor's rate increases the density of chemical species (H_2O) which dissociate around 3500 K and decreases the density of chemical species (N_2) which dissociate around 7500 K. Sound velocity increases with temperature and increases when the rate of water vapor increases in the

plasma. The increasing is more important for temperatures above 3500 K. The knowledge of thermodynamic properties allows the determination of the density of energy and the power flow. For temperature less than 3500 K and above 7000 K, the density of energy decrease when the rate of water vapor increase in the mixture and for temperature between 3500 K and 7000 K ($3500\text{ K} < T < 7000\text{ K}$), the density of energy increases when the rate of water vapor increases in the mixture. The power flow decreases, with the rate of water vapor in the mixture for temperature less than 3500 K and increases with the rate of water vapor for temperature above 3500 K. The increasing is important for temperature ranging from 3500 K to 8500 K.

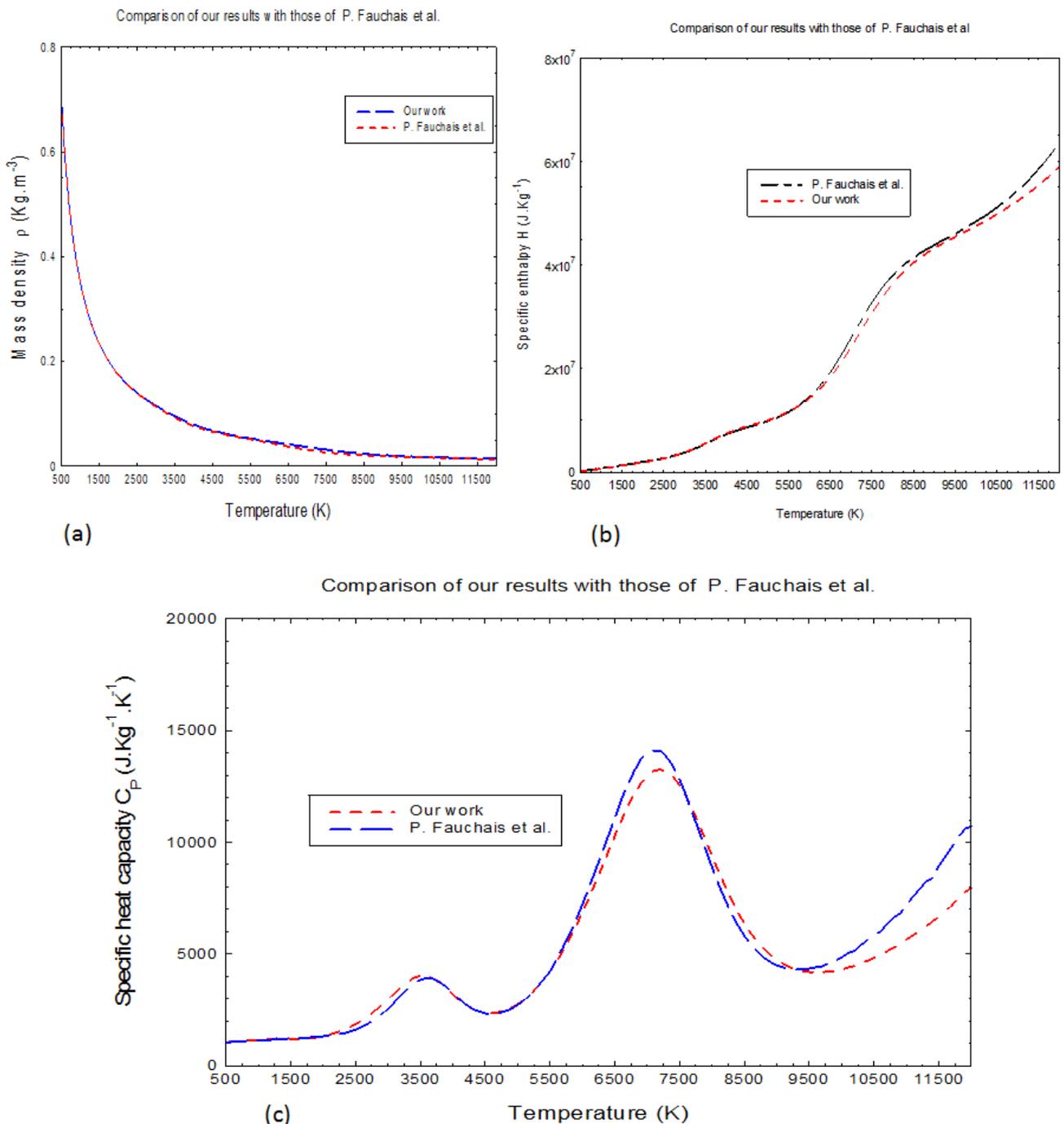


Figure 2. Comparison of our results of dry air plasma with those of P. Fauchais and al. [35]: (a) Mass density versus temperature, (b) Specific enthalpy versus temperature and (c) Specific heat capacity versus temperature

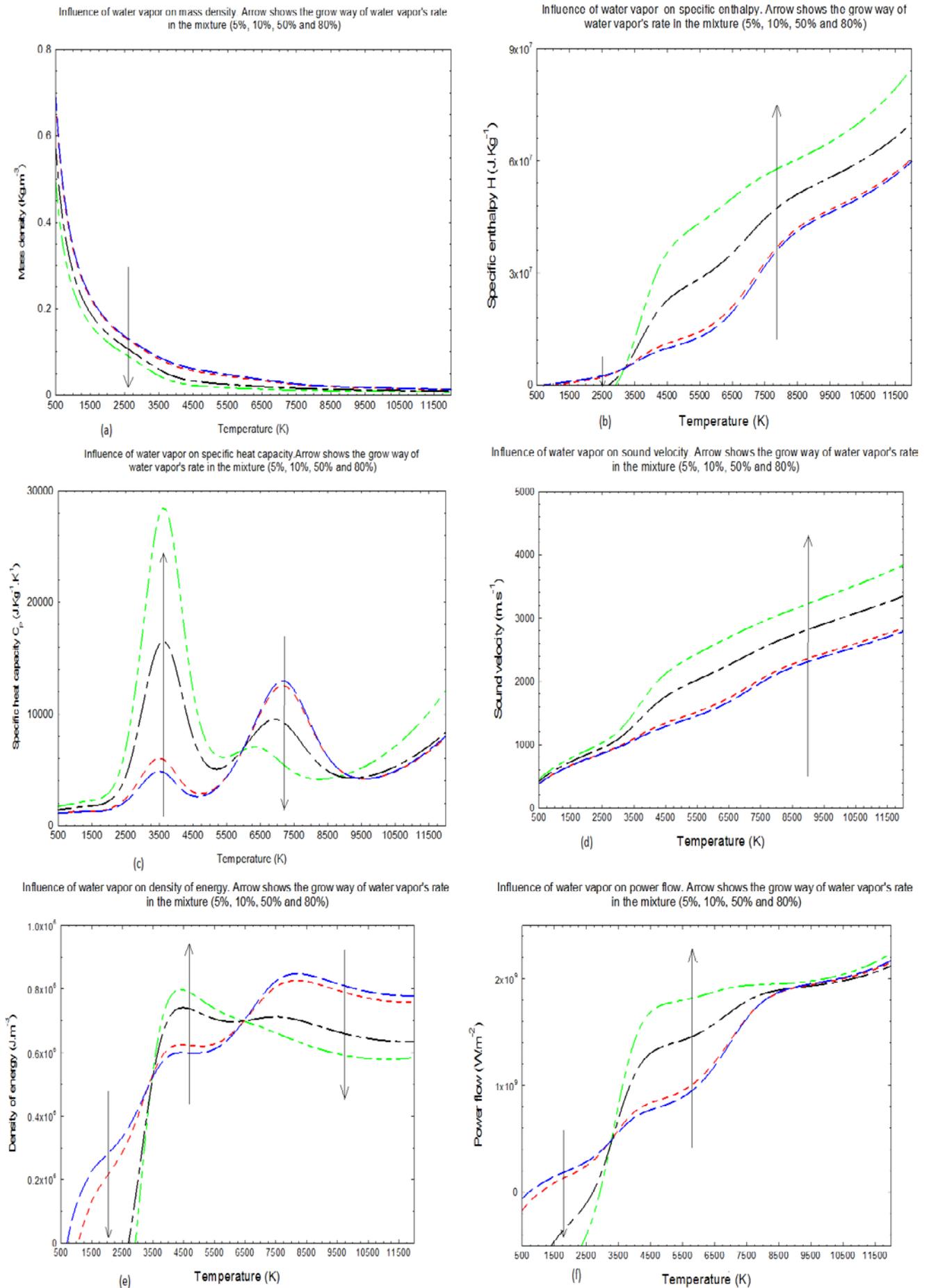


Figure 3. (a) Mass density versus temperature, (b) Specific enthalpy versus temperature, (c) Specific heat capacity versus temperature, (d) Sound velocity versus temperature, (e) Density of energy versus temperature and (f) Power flow versus temperature

4. Conclusion

In the present work, our objectives has been to show the influence of vapor water on the thermodynamic properties of air and water vapor mixtures in the temperature range 500 K to 12 000 K. These thermodynamic properties are necessary to get the density of energy and power flow. We used the minimization of the Gibbs free energy method to calculate the numerical density of the different chemical species which are also use to calculate the thermodynamic properties. We considered the following plasmas: 95 % air - 5 % water vapor; 90% air - 10 % water vapor; 50 % air - 50 % water vapor and 20% air - 80 % water vapor.

The results show that, the mass density decreases when the percentage of water vapor increase in the mixture, enthalpy increase with the rate of water vapor. Specific heat capacity increases for temperature low than 6000K and decreases between 6000K and 9000K. The increasing of the rate of water vapor in the mixture decreases the density of energy for temperatures less than 3500 K and above 7000 K. The decreasing of density of energy is important to contain the energy in the mixture. Also the power flow increases with the rate of water vapor for temperatures above 3500 K. This increasing of the power flow is important to cool the medium. The curve of density of energy and power flow of the plasma versus the rate of vapor water are a good indicator for electric arc extinction. So the increasing of the water vapor in the air can be interesting for power cut in circuit breakers.

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