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Composition of Air-Water Vapor Mixtures at Low Temperatures

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ABSTRACT: The composition of plasmas formed of air and water vapor mixtures is calculated in the temperature range from 500 to 12000 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. The results are presented and discussed. The results of the equilibrium composition show in particular that the concentration of hydrogen increases with the proportion of water vapor in the mixture. It is could improve the performance of plasma during current breaking.

KEYWORDS: Plasma, equilibrium composition, Gibbs free energy

I. INTRODUCTION

Air and water are among the most abundant matters of our immediate environment. Also the air and water vapor are present in many applications of the electric arc and plasmas. We can cite atmospheric re-entry spacecraft [1], the electric arc interaction-surface [2], the purification of gaseous rejection and detection methods in aqueous medium [3]. Air and water have intervened in several works [3, 4, 5, 6, 7]. Our literature reviews have revealed that there is very little work on thermal plasmas of mixtures of air and water vapor. Nevertheless, we can cite the work of S. Cayet [8], those of R. Hannachi [3] and finally those of Kagoné and al. [1, 9]. Several theoretical and experimental studies in thermal plasma have been realized [10-14]. Our study concerns the current breaking through the electric arc. Indeed, the current breaking in some circuit breakers is obtained by separating electrodes in air or compressed air [1]. At the opening of these contacts, it creates an electric arc which interacts with surrounding gas and creates the plasma of this gas. Previous studies have shown that the presence of hydrogen in the plasma improves his characteristics during the current breaking [15, 16]. This hydrogen can be brought in the mixture by water vapor. So, the water vapor present in the atmospheric air, particularly in areas of high humidity should already have an influence on the proprieties of the plasma in the air circuit breakers. This theoretical study concern four plasmas of mixtures of air and water vapor, the proportions are: 93% air - 7% water vapor, 80% air - 20% vapor water, 50% air - 50% water vapor and 20% air - 80% water vapor. We suppose that the air is constituted by 20% of oxygen and 80% of nitrogen and that the plasma is in local thermodynamic equilibrium (LTE). The first step to determine the characteristics of plasma is to know the equilibrium composition. This theoretical study concerns the determination of equilibrium composition of plasma formed of mixtures of air and water vapor in the temperature range from 500 K to 12000 K. These studies complete the one of Kagoné and al. [1] in the temperature range 5000 K - 30000 K. We compare our results with those of Kagoné and al. [1] in the table 2. Then, we present and discuss our results of equilibrium composition of plasma formed of mixtures of air and water vapor.

II. CALCULATION OF PLASMA COMPOSITION

We tank into account in our calculation forty following chemical species: electrons(e^-),H,H^-,H^+,N,N^+,N^{++},O,O^-,O^+,O^{++},H_2, H_2^-, H_2^+, N_2, N_2^-, N_2^+, NH, NH^-, NH^+, NO, NO^-, NO^+, O_2, O_2^-, O_2^+, OH, OH^-, OH^+, O_3, H_2O, N_2O, NH_3, N_2O_3, HNO_2, HO_2, N_2O_4, H_2N_2, N_2O_5, HNO_3.

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A. DETERMINATION OF EQUILIBRIUM COMPOSITION

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 [1, 16-18] and that based on the minimization of the Gibbs free energy [19-22]. We use the minimization of Gibbs free energy to determine the composition versus the temperature at atmospheric pressure of the considered plasma. At temperature T and pressure P the Gibbs free energy is written as:

$$G = \sum_{i=1}^{N} n_i \left(\mu_i^o + RT_i \ln\left(\frac{n_i}{\sum_{j=1}^{N} n_i} \right) + RT_i \ln\left(\frac{P}{P^o} \right) \right) \quad (1)$$

where n_i is the mole number of chemical species, N is the number of different chemical species presented in the plasma and gas, μ_i^o is the chemical potential of i species at standard pressure P^0 ($10^5 P_a$), R is the molar gas constant. T_i is the temperature of each chemical species i and is equal to the Temperature T in the considered case since we assume thermal equilibrium.

B. ELECTRICAL NEUTRALITY AND NUCLEI CONSERVATION

The electrical neutrality and the nuclei conservation in the plasma is written as:

$$\sum_{i=1}^{N} a_{ij} n_i = b_j \qquad j = 0, \ldots, m \quad (2)$$

Where m is the number of different nuclei equal to three in our case (H, O, N). j=0 is devoted to the electrical neutrality in the plasma. a_{ij} Represents the nucleus number of type j for particle i ; b_j is equal to the number of different nucleus types in the initial mixture; a_{i0} represents the number of elementary charge of particle i ; so electrical neutrality impose $b_0 = 0$.

C. DALTON LAW

The Dalton's law is written as:

$$P - \Delta P = \sum_{i=1}^{N} N_i RT_i \quad (3)$$

Where N_i is the molar density of i chemical species and ΔP [16, 23-25] is the pressure correction due to coulomb interaction.

$$\Delta P = \frac{1}{24\pi\varepsilon_0 l_d} \sum_{i=1}^{N} q_i^2 n_i \quad (4)$$

With l_d is the Debye length defined by: $l_d = \left(\varepsilon_0 R \sum_{i=1}^{N} \frac{T}{q_i^2 n_i} \right)^{1/2}$ (5)

Where ε_0 is the vacuum permittivity and q_i the electrical charge of species i.

D. NUMERICAL METHOD

The mole number must be non-negative and satisfy the conservation of nuclei and electrical neutrality, so the different values must satisfy both conditions:

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$$\begin{cases} n_i \geq 0 & \forall i \\ \sum_{i=1}^{N} a_{ij} n_i = b_j & j=0,\cdots,m \end{cases} \quad (6)$$

By introducing the Lagrange multipliers π_k to take the physical conditions (2) into account and using a Newton-Raphson numerical method, the following system can be obtained [7, 21, 25]:

$$\begin{pmatrix} \frac{RT}{n_1} & \cdots & 0 & a_{1,0} & \cdots & a_{1,3} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & \frac{RT}{n_N} & a_{N,0} & \cdots & a_{N,3} \\ a_{1,0} & \cdots & a_{N,0} & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{1,3} & \cdots & a_{N,3} & 0 & \cdots & 0 \end{pmatrix} \begin{pmatrix} \Delta n_1 \\ \cdots \\ \Delta n_N \\ \Delta \pi_0 \\ \cdots \\ \Delta \pi_3 \end{pmatrix} = \begin{pmatrix} -\mu_1^0 - RT \ln \frac{n_1}{\sum_{i=1}^{N} n_i} - RT \ln \frac{P}{P_0} - \sum_{j=0}^{3} \pi_j a_{1,j} \\ \cdots \\ -\mu_N^0 - RT \ln \frac{n_1}{\sum_{i=1}^{N} n_i} - RT \ln \frac{P}{P_0} - \sum_{j=0}^{3} \pi_j a_{N,j} \\ -\sum_{i=1}^{N} n_i a_{i,0} + b_0 \\ \cdots \\ -\sum_{i=1}^{N} n_i a_{i,3} + b_3 \end{pmatrix} \quad (7)$$

The dimension of this linear system is N+4. The coefficients b_j depend on the initial volume percentages in the mixture. We calculate the chemical potential of each particle by the data obtained in the works of André and al. and using the formula [7]:

$$\mu_i = h_i - Ts_i + E_i \quad (8)$$

Where h_i is the specific enthalpy, S_i is the specific entropy and E_i is the formation enthalpy of the chemical species. For the polyatomic molecules their data are obtained in the JANAF tables [26]. The chemical potential of each particle can be determined by the partition function [26, 27]. Then the values of new molar number and the Lagrangian multipliers are calculated with:

$$\begin{cases} n_i = n_i + \lambda \Delta n_i & \forall i \in [1, N] \\ \pi_j = \pi_j + \lambda \Delta \pi_j & \forall j \in [0, 3] \end{cases} \quad (9)$$

The parameter λ is the highest value included between zero and one that satisfies the following conditions:

$$n_i = n_i + \lambda \Delta n_i \succ 0 \quad \forall i \in [1, N] \quad (10)$$

This step avoids obtaining of negative new mole number that appears when they are far from the solution.
The new values of the molar number and Lagrangian multipliers are used for a new calculation cycle. The convergence is considered to be reached when the values Δn_i satisfy the following relation:

$$\frac{\Delta n_i}{n_i} \prec 10^{-15} \quad \forall i \in [1, N] \quad (11)$$

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III. RESULTS AND ANALYSES

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

Table. 1: Plasmas study.

Plasma name	Notation	Values of b_i			
Plasma of 93% air - 7% water vapor	Mix.1	0	7	22,1	74,4
Plasma of 80% air - 20% water vapor	Mix.2	0	10	13	32
Plasma of 50% air - 50% water vapor	Mix.3	0	10	7	8
Plasma of 20% air - 80% water vapor	Mix. 4	0	20	11	4

A. TEST OF CALCULATION PROGRAM

We first tested our program of calculation by comparing our results with those of Kagoné and al. [1] in Table.2. Our values and those of this author are in good agreement with a relative error less than 10 %. These discrepancies are probably due to the data used in the calculations method. We used the method of minimization of the Gibbs free energy and this author has used the law of mass action. Also this author does not take the same chemical species into account, especially the polyatomic species.

Table.2: Comparison of our results and those of A. K. Kagoné [17]

Species	**Results of Kagoné [17]**			**Our results**		
	8000 K	9000 K	10000 K	8000 K	9000 K	10000 K
e^-	2.17E+21	6.76E+21	1.69E+22	2.18 E +21	6.71 E +21	1.67 E +22
H	1.72E+23	1.47E+23	1.28E+23	1.71 E +23	1.47 E +23	1.28 E +23
H^+	3.74E+20	1.12E+21	2.69E+21	3.73 E +20	1.11 E +21	2.62 E +21
N	4.86E+23	4.58E+23	4.05E+23	4.89 E +23	4.59 E +23	4.05 E +23
N^+	1.16E+21	4.23E+21	1.11E+22	1.14 E +21	4.21 E +21	1.11 E +22
O	2.23E+23	1.91E+23	1.67E+23	2.22 E +23	1.91 E +23	1.67 E +23
O^+	4.37E+20	1.30E+21	3.11E+21	4.17 E +20	1.25 E +21	2.98 E +21
H_2	1.08E+19	4.07E+18	1.83E+18	1.20 E +19	4.52 E +18	2.02 E +18
N_2	3.20E+22	5.47E+21	1.12E+21	2.91 E +22	5.10 E +21	1.08 E +21
NO	5.68E+20	1.55E+20	4.93E+19	5.63 E +20	1.58 E +20	5.26 E +19
O2	9.26E+18	3.16E+18	1.31E+18	9.41 E +18	3.23 E +18	1.34 E +18

B. COMPOSITION OF MIXTURES PLASMAS OF AIR AND WATER VAPOR.

In the figures.1**,** we represent respectively the concentration of chemical species versus temperature at atmospheric pressure and local thermodynamic equilibrium (LTE) of the following plasmas: 93% air - 7% water vapor, 80% air - 20 % water vapor, 50 % air - 50 % water vapor and 20 % air - 80 % water vapor. We note that the numerical density of the individual particles of plasma Mix.1, Mix.2, Mix.3 and Mix.4 evolve likewise. On the four (4) figures, 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 molecules: N_2, O_2 and H_2O. 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: N_2, O_2, H_2O, NO, OH, H_2, 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^-.The analyses of the curves show that the numerical density of the neutral particles H, O and N depend of the percentage of the initial mixture. 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 [28]. For high temperature (T > 5000 K), the ionization of the atoms H, O and N take place to the production of electrons. In plasma Mix.1 and Mix.2, the ionization of atom N contributes most to the production of electrons. In plasma Mix.3, the ionization of atoms N and H contribute more to the production of electrons. In plasma Mix.4 the ionization of atom O contributes most to the production of electrons. The water molecule H_2O dissociates around 3000 K. O_2, H_2 and OH molecules dissociate around 3500 K. The particle NO dissociates around 5000 K .The diazote molecule N_2 dissociate around 7500 K. On all these figures, we note that the polyatomic species: O_3, H_2O, N_2O, NH_3, N_2O_3, HNO_2, HO_2, N_2O_4, H_2N_2, N_2O_5 and HNO_3 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^-, O_2^-, N_2^- and H_2^- species appear with low concentration ($n_i < 10^{+19}$). However, these particles could have a significant influence

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on the electrical conductivity of the plasma, because they capture electrons and decrease their mobility in the plasma. We remark that the concentration of hydrogen (H) increases with the initial proportion of water vapor in the mixture.

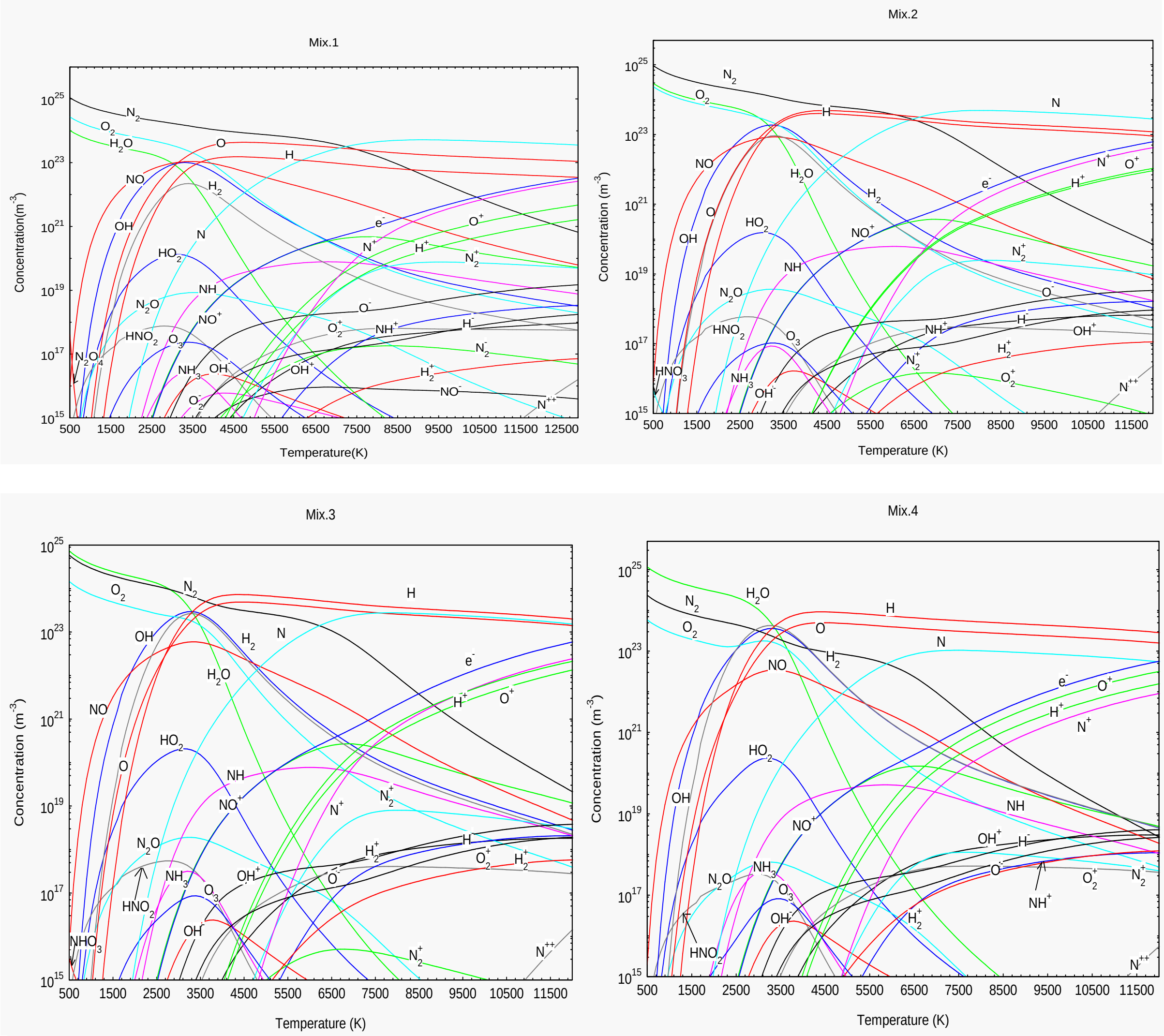

Figure.1. Concentration versus temperature of different chemical species of plasmas at atmospheric pressure and local thermodynamic equilibrium: plasma Mix.1, plasma Mix.2, plasma Mix.3 and plasma Mix.4.

C. EFFECT OF THE PERCENTAGE OF WATER VAPOR ON THE PLASMA COMPOSITION.

To see the influence of the percentage of water vapor on the chemical composition of the plasma, we considered the following plasmas: Mix.1, Mix.2, Mix.3 and Mix.4. We have choose to interest at the concentration of the following chemical species: e^-, H, H^+. Figure.2 gives the concentrations versus temperature of the following chemical species: (e^-, H^+ and H). This figure shows that the numerical density of electron decreases when the rate of water vapor increases in plasma at the temperature below 8000 K and above 8000 K she varies very little. This is due to the fact that at low temperatures the ionization of NO is the production source of electrons and his concentration decreases when the rate of water vapor increases in the plasma. While in the high temperature, electron density depends very little on the nature of the mixture, since the plasma is nearly completely ionized. The numerical density of hydrogen atom (H) grows with proportion of the water vapor in the mixture.

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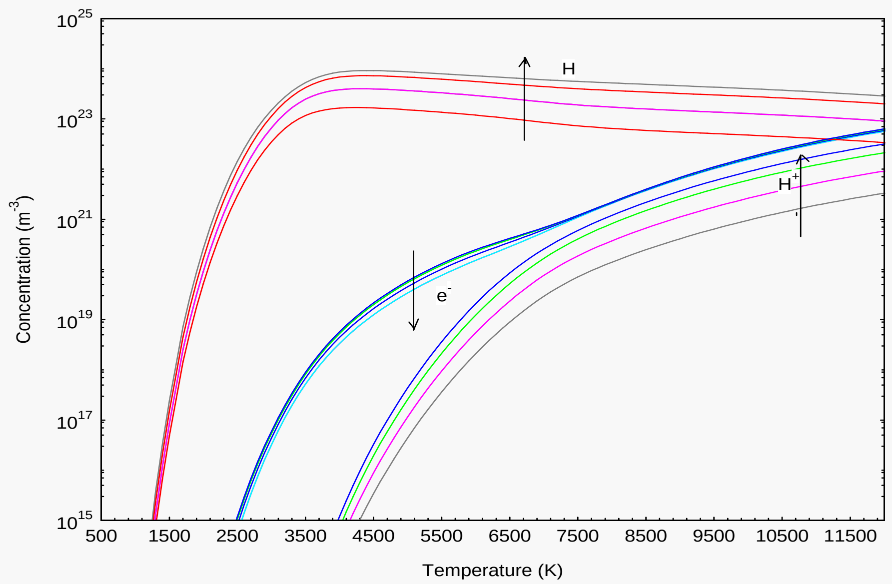

Figure.2: Influence of water vapor on the concentration of the chemical species at atmospheric pressure and LTE. Concentration versus temperature of chemical species of plasmas Mix.1, Mix.2, Mix.3 and Mix.4: (e^-, H and H^+). Arrow shows the grow way of water vapor's rate in the mixtures (7%, 20%, 50% and 80%).

IV. CONCLUSION

In the present work, it has been question to determine the chemical composition of air and water vapor mixtures in the temperature range 500 K to 12 000 K. We used the minimization of the Gibbs free energy method to calculate the numerical density of the different chemical species versus temperature. The results show that the numerical density of hydrogen (H) increases with the percentage of water vapor. In all plasmas, the electrical neutrality is mainly made at low temperature between e^- and NO^+. The previous studies [29] have shown that in the case of power cut, more concentration of hydrogen is high; more the plasma has good performance for the extinction of electric arc. So, the increasing of the water vapor in the air can be interesting for power

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