Calculation of the Chemical Composition of Air - PMMA Mixtures Thermal Plasmas

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Abstract: Knowledge of the chemical composition of plasma is necessary for calculations and modeling in thermal plasmas. Indeed, from the knowledge of this composition we can calculate the thermodynamic properties, the transport coefficients and the radiative properties of a plasma medium. In this work, we propose to study at thermodynamic equilibrium the influence of pressure and of the PMMA polymer on the composition of the plasma of the Air - PMMA gas mixture. We are studying in particular the evolution of the density of the species created in this plasma as a function of temperature (5000 - 30000 K) and pressure (1 bar - 10 bar) for variable mixtures at thermodynamic equilibrium. When we want to take into account a large number of chemical species in the plasma, two main methods are usually used, one is based on the law of mass action and the other on the minimization of Gibbs’ free enthalpy. In our study, we used the mass action law method to calculate the composition of plasma. The results obtained show that when the plasma is in thermodynamic equilibrium the densities of the different species present in the plasma are only a function of the temperature, the pressure and the percentage of the polymer in the mixture.

Keywords: Electric Arc, Plasma, Chemical Composition, Density, Polymer, Circuit Breaker

1. Introduction

The electric arc which is generally defined as a high current electrical discharge has a wide variety of applications these days. Due to the wide range of its applications, it has given rise to numerous research works both on an experimental and theoretical level [1-35]. Among its applications, we can cite, among other things, lighting, welding, cutting, waste treatment and cutting of electric current. Indeed, the interruption of the electric current in certain switchgear, in particular the circuit breaker, is done from the electric arc. To cut the electric current, the opening of the circuit breaker contacts creates an electric arc which interacts with the surrounding environment. If in most applications, the arc must be maintained for as long as possible, its rapid extinction is sought in breaking devices. In fact, they are designed to provide manual or automatic control of electrical circuits (contactors) as well as protection of installations against short circuits (circuit breaker).

Certain cutting techniques are based on the rapid elongation of the arc between the contacts and others, on a rolling of the arc between two insulating parts. Numerous theoretical [3-4, 13, 18, 25, 27-35] and experimental [3, 10] studies have already been carried out on polymers. From studies carried out on laminated arcs with ablative walls [2-3], it appears that the PMMA polymer has interesting characteristics for breaking the electric current.

Our study is part of the interruption of the electric current by means of the electric arc used as energy dissipater by heat exchanges with the surrounding environment. As the cutting technique in air and compressed air [36] is widely used in low and medium voltage circuit breakers, in this work, we want to
study the influence of the PMMA polymer on air breaking performance.

The breaking performance is partly linked to certain characteristics of the plasma formed in the circuit breaker at the time of breaking. Determining any characteristic of a plasma begins with knowing the equilibrium composition of the plasma.

This article is therefore devoted to the calculation of the equilibrium composition of plasmas of Air - PMMA mixtures at thermodynamic equilibrium. In addition to pure air and pure PMMA, the mixtures concerned are: 80% Air - 20% PMMA; 50% Air - 50% PMMA; 20% Air - 80% PMMA. The temperature range goes from 5000K to 30000K for pressures of 1 bar; 2 bar; 5 bar; 8 bar and 10 bar.

2. Calculation Assumptions

The calculation of the chemical composition of the Air - PMMA plasma constitutes a first approach to the environment studied, allowing to know the evolution of the density of the different particles present, as a function of the temperature and the PMMA percentage. It is moreover necessary for the calculation of the thermodynamic properties and the transport coefficients of the plasma medium.

The calculation of the chemical composition was made with the following assumptions:

(i) The plasma is at local thermodynamic equilibrium;
(ii) The composition of the air is: oxygen 20%, nitrogen 80%;
(iii) The percentages of the various mixtures are percentages by volume.

PMMA is the abbreviation for the polymer of common name Plexiglas, composed of polymethyl methacrylate and whose chemical formula is C₅H₈O₂. The basic atoms of air are oxygen (O) and nitrogen (N) and those of PMMA are carbon (C), hydrogen (H) and oxygen (O). The basic atoms in the Air - PMMA mixture are therefore carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). Given the range of temperatures considered (5000K to 30000K), the different chemical species that we have taken into account in the composition of plasmas are electrons, diatomic molecules, neutral atoms and their corresponding ions charged once or twice; be the following 32 particles.

\[
\begin{align*}
\text{e} & , \text{H} & , \text{N} & , \text{O} & , \text{C}_2 & , \text{H}_2 & , \text{N}_2 & , \text{O}_2 & , \text{C}- & , \text{H} & , \text{N} & , \text{O} & , \text{C}^+ & , \text{H}^+ & , \text{N}^+ & , \text{O}^+ & , \text{C}_2^+ & , \text{H}_2^+ & , \text{N}_2^+ & , \text{O}_2^+ & , \text{C}^{2+} & , \text{N}^{2+} & , \text{O}^{2+} & .
\end{align*}
\]

In the rest of the article, the numerical density of the electrons will be represented by \(n_e\) and those of other particles by their corresponding chemical symbols. As an example, the numerical density of hydrogen atoms will be noted \(H\).

3. Method of the Plasma Chemical Composition Calculation

Calculation of the chemical composition of plasma is done by the method based on the law of mass action. It is done using a system of equations, the number of which is determined by the number of chemical particles taken into account in the composition of the plasma. In this study, the number of chemical particles taken into account in the composition of the plasma being equal to 32, then we will have a system of 32 equations with 32 unknowns. Some of these equations require knowledge of the internal partition functions of the different particles. Writing the equilibrium constants at constant pressure for each of the reactions as a function of the partition functions on the one hand and the numerical densities of the chemical particles on the other hand, provide a number equations of the system.

Solving the system of equations using the Newton-Raphson resolution method gives access to the chemical composition of the plasma.

Indeed, at thermodynamic equilibrium, the numerical densities of the different particles contained in the plasma are perfectly determined from a system of equations obtained by applying to the plasma the fundamental laws of thermodynamic.

(i) Ideal gas law

It assumes that all the plasma and each of its constituents behaves as a perfect gas. So it says:

\[
P = kT \sum_{i=1}^{v} n_i
\]

Where \(P\) is the total pressure, \(n\) the numerical density of the species \(i\), \(k\) the Boltzmann constant and \(v\) is the number of particles.

(ii) Law of electrical neutrality

It is a law which translates the fact that the plasma is electrically neutral on the macroscopic scale:

\[
n_e - \sum_{i=1}^{v} Z_i n_{i_z} = 0
\]

Where \(n_{i_z}\) is the numerical density of heavy particles \(i\) with the charge \(Z_i\), \(n_e\) the numerical density of the electrons.

(iii) Saha-Eggert's laws

They govern the balance between the number of atoms, ions and electrons per unit volume. For a reaction of the type \(A \rightarrow A^+ + e^-\), Saha-Eggert's law is written:

\[
S_A = \frac{n_{e/z}}{n_A} = 2 \left( \frac{2 \pi m_e kT}{h^2} \right)^{3/2} \left( \frac{Q_{\text{int}}}{Q_{\text{int}}^A} \right)^{3/2} \exp \left( -\frac{E_A - \Delta E_A}{kT} \right)
\]

Where \(m_e\) is the mass of the electron, \(n_A^+\) and \(n_A\) are the numerical densities of the particles respectively \(A^+\) and \(A\). \((Q_{\text{int}}^A)\) is the internal partition function of the specie \(A^+\) and \(Q_{\text{int}}\) that of the particle \(A\), \(E_A\) is the ionization energy of \(A\), \(\Delta E_A\) is the reduction of the ionization energy due to a phenomenon of plasma polarization at the macroscopic level. It depends on the charge and the numerical
densities of the charged particles, as well as on the plasma temperature. 

$S_A$ is called the ionization equilibrium constant. The specie $A$ can be either a neutral particle or a charged particle. The expression of the ionization potential reduction proposed by Capitelli et al [3] is written:

$$\Delta E_J = 2(Z_J + 1)e^3 \left( \frac{\pi}{KT} \right)^{1/2} \left( n_e + \sum_i Z_i^2 n_i \right)$$  \(4\)

The summation relates to all the heavy charged particles. $Z_j$ is the number of charges of the specie $j$.

(iv) Laws of Guldberg and Waage

These equations translate the dissociation-recombination equilibria existing in the plasma. For an equation of the type $AB \rightarrow A + B$ (A may be the same as B); she is written:

$$K_{AB} = \frac{n_A n_B}{n_{AB}} = \left( \frac{2\pi kT}{m_{AB}} \right)^{3/2} \frac{(Q_{int})_A}{(Q_{int})_{AB}} \exp \left( -\frac{E_{d}}{kT} \right)$$  \(5\)

Where $n_A, m_A, (Q_{int})_A$ are respectively the numerical density, the mass and the internal partition function of the specie $A$. $E_d$ is the dissociation energy of the particle $AB$. $K_{AB}$ is called the dissociation equilibrium constant.

(v) Equations of basic elements proportions

The equations of proportions are equations which express the content of basic elements of the plasma. The basic elements are neutral atoms ($C, H, O, N$) contained in the chemical formulas of gases giving rise to plasma.

4. Particles Internals Partition Functions

The partition functions of the different particles are essential for calculating the equilibrium composition of the plasma. They can be determined either from the literature (by numerical smoothing of the tabulated values), or using the formulas below.

(i) Internals partition functions of monoatomic particles

The relationship below is the general expression of the internal partition function of monoatomic species.

$$Q_{int}(T) = \sum_n g_n \exp \left( -\frac{E_n}{kT} \right)$$  \(6\)

The summation relates to all energy levels $E_n$ of statistical weight $g_n$. So that it is not divergent, we limit ourselves to $E_n \ll E_i - \Delta E_i$, $E_i$ being the ionization energy of the particle. The internal partition functions are generally known and tabulated according to the temperature and the reduction of the ionization energy $\Delta E_i$.

For the electrons we have: $Q_{int} = 2$

(ii) Internals partition functions of diatomic particles

We can determine the internal partition functions of diatomic particles from Herzberg’s formula

$$Q_{int} = \sum_n g_{max}^n Q_n$$  \(7\)

Where $Q_n$ is the partition function for the electronic state $n$ of the molecule and defined by:

$$Q_n = \frac{g_n \exp \left( -\frac{E_n}{kT} \right)}{kT}$$  \(8\)

Where $g_n, E_n, \beta_n, \omega_n$ are respectively the statistical weight, the energy, the constant of rotation and the constant of vibration of the state $n$ of the molecule. $\sigma$ is a factor of symmetry ($\sigma = 1$ for hetero nuclear molecules and $\sigma = 2$ for homo nuclear). $h$ is Planck’s constant and $c$ the speed of light.

The parameters $\omega_n, \beta_n, \omega_n$ are defined by:

$$\omega_n = \omega_c - \chi_c \omega_c$$  \(9\)

$$\beta_n = \beta_c - \frac{\alpha_c}{2}$$  \(10\)

$$E_n = T_c + \frac{1}{2} \left( \omega_c - \frac{1}{2} \chi_c \omega_c \right)$$  \(11\)

$\omega_c, \omega_c, \chi_c, \beta_c, \alpha_c$ are constants depending on the state of vibration and rotation for a given state in the approximation of the harmonic oscillator and the rigid rotator. $T_c$ is the electronic energy of the state considered. These are known and tabulated constants. The values of $T_c, \omega_c, \beta_c, \chi_c$ and $\alpha_c$ for each electronic state $n$ of certain diatomic molecules are given by Herzberg. For other diatomic particles, the values of the different constants are recorded in the tables of Janaf [3].

In the expression $Q_{int}$, $n_{max}$ is chosen as the electronic energy state $E_{n_{max}}$ lower than the dissociation energy of the molecule considered.

5. Calculation of the Plasma Chemical Composition

The total number of chemical particles taken into account in the composition of the plasma is thirty-two (32). It is therefore necessary to constitute a system of thirty-two (32) equations with thirty-two (32) unknowns.

(i) Formulation of the system of equations

The numerical densities of the chemical particles taken into account in the plasma are determined using a system of equations formed from:

a) the ideal gas law,

b) the law of electrical neutrality,

c) Saha-Eggert laws,
d) Guldberg and Waage laws, 
e) the proportions of the species present.

The ideal gas law gives the first equation:

\[ P = n k T \]

where \( n \) is the total numerical density of the particles present in the plasma and \( k \) the Boltzmann’s constant. We have:

\[
n = n_e + C^+ + C^{2+} + C_2^+ + C_2^{2+} + C_3^+ + H + H^+ + H_2 + H_2^+ + O + O^-
\]

\[+O^{2+} + O_2^+ + N + N^+ + N^2+ + N_2 + N_2^+ + CH + CO + CN + OH + HN + NO + CH^+ + CO^+ + CN^+ + OH^+ + HN^+ + NO^+\]

With \( n_e \) the numerical density of electrons.

The law of electrical neutrality gives the following second equation:

\[
n_e = C^+ + 2C^{2+} + C_2^+ + H^+ + H_2^+ + O^+ + 2O^{2+} + O_2^+ + N^+ + 2N_2^+ + CH^+ + CO^+ + CN^+ + OH^+ + HN^+ + NO^+\]

Saha-Eggert’s laws define 17 equilibrium constants corresponding to the 17 ionization reactions taking place in plasma. Consequently, the relation (3) applied to the 17 ionization reactions gives 17 equations.

The laws of Guldberg and Waage through the written relation for the dissociation of diatomic particles \( C_2, H_2, O_2, N_2, CH, CO, CN, OH, HN \) and \( NO \), allows to establish 10 equations relating to the equilibrium of the ten (10) dissociation reactions taking place in the plasma.

The above laws thus provide a system of 29 equations with 32 unknowns.

To the system, we add additional equations defining the proportions of carbon atom (\( x \)), hydrogen atom (\( y \)), oxygen atom (\( z \)) and nitrogen atom (\( t \)).

In case the variables \( x, y, z \) and \( t \) are all non-zero, we can write three (3) independent proportion equations. Is:

\[
x = \frac{2C_2 + 2C_2^+ + C^2 + C^{2+} + C_2^{2+} + CH + CO + CN + CH^+ + CO^+ + CN^+}{2H_2 + 2H_2^+ + H + H^+ + CH + OH + HN + CH^+ + OH^+ + HN^+}
\]

\[
y = \frac{2H_2 + 2H_2^+ + H + H^+ + CH + HO + HN + CH^+ + HO^+ + HN^+}{2O_2 + 2O_2^+ + O + O^+ + O^{2+} + CO + OH + ON + CO^+ + OH^+ + ON^+}
\]

\[
z = \frac{2O_2 + 2O_2^+ + O + O^+ + O^{2+} + CO + OH + ON + CO^+ + OH^+ + ON^+}{2N_2 + 2N_2^+ + N + N^+ + N^2+ + CN + NH + NO + CN^+ + NH^+ + NO^+}
\]

We thus obtain a system of thirty - two (32) equations with thirty - two (32) unknowns. The unknowns are the numerical densities of the particles taken into account in the plasma.

(ii) Solving the system of equations

The system of thirty - two (32) equations with thirty - two unknowns (32) obtained is a nonlinear system. Using the relations defining the equilibrium constants of ionization and dissociation, we can by substitution reduce the system to a nonlinear system of five (5) equations with five (5) unknowns. The five (5) unknowns are the numerical densities of the electrons (\( n_e \)), carbon atoms (\( C \)), hydrogen atoms (\( H \)), oxygen atoms (\( O \)) and nitrogen atoms (\( N \)). The resolution of the system is then carried out using an iterative method (Newton-Raphson method), based on the linearization of the nonlinear system. We then obtain the numerical densities \( n_e, C, H, O \) and \( N \), and therefore the concentrations of the other particles.

6. Results and Discussions

The equilibrium chemical composition was calculated for plasmas of the following different mixtures of air and PMMA:

a) 100% Air,  
b) 80% Air - 20% PMMA,  
c) 50% Air - 50% PMMA,  
d) 20% Air - 80% PMMA,  
e) 100% PMMA.

The temperature range goes from 5000K to 30000K for pressures of 1 bar; 2 bar; 5 bar; 8 bar and 10 bar.

Figures 1 to 5 respectively give the results of the equilibrium composition calculations of plasmas of: 100% Air; 80% Air - 20% PMMA; 50% Air - 50% PMMA; 20% Air - 80% PMMA and 100% PMMA at thermodynamic equilibrium and at a pressure of 1 bar. These different figures give the variations of the five plasmas compositions as a function of temperature, at a pressure of 1 bar. The various results obtained show that whatever the mixture, the composition of the plasma obtained changes in three phases as a function of the temperature. The first phase is characterized by the predominance of diatomic particles for temperatures below 7500 K. A second phase between the temperatures of 7500 K and 15000K marked by a strong presence of neutral monoatomic particles coming from the reactions of dissociation of diatomic particles. At the end, the third phase going from 15000 K to 30000 K where the neutral particles gradually become negligible compared to the electrons and the ionized particles. For temperatures above 25000 K, the strong presence of charged particles makes it possible to consider the plasma as almost completely ionized.

By observing all of the curves in Figures 1 to 5, the following remarks can be made:

1) The numerical densities of neutral diatomic particles decrease rapidly with temperature. This decrease is explained by the fact that these particles have low dissociation energy values.

2) For plasmas containing the elements carbon and oxygen, we note that the numerical density of the CO particle is relatively high at low temperatures. This is explained by the fact that this particle has a high dissociation energy. This results in low numerical densities of carbon atoms C and oxygen O, for temperatures below 7000 K.

3) It should be noted in general that for mixtures containing the elements carbon, hydrogen, oxygen and nitrogen, the numerical densities of the neutral atomic particles C, H, O and N present in the plasma depend on their initial percentage. But in particular, the numerical density of the hydrogen atom H remains the most important in the plasmas of these mixtures. This is because the diatomic
particles containing hydrogen have the lowest dissociation energies.

4) The production of electrons at low temperature is entirely due to the ionization of carbon C for mixtures containing this element. This is related to the low value of the ionization energy of carbon compared to that of other neutral monoatomic particles. On the other hand, for 100% Air plasma where there is no carbon element, the production of electrons at low temperature is due to the ionization of the diatomic particle NO.

5) Apart from the 100% Air plasma, the ionization of the hydrogen atoms H constitutes the most important part in the numerical density of the electrons in the plasma, for temperatures higher than 15000 K. For the plasma of 100% Air, it is the ionization of the nitrogen atoms N which represents the most important part. In all mixtures, the contribution of twice ionized particles is appreciable only at very high temperatures.

Figure 1. Variation of the 100% Air plasma composition as a function of temperature, at a pressure of 1 bar.

Figure 2. Variation of the composition 80% Air - 20% PMMA plasma as a function of temperature, at a pressure of 1 bar.

Figure 3. Variation of the 50% Air - 50% PMMA plasma composition as a function of temperature, at a pressure of 1 bar.

Figure 4. Variation of the 20% Air - 80% PMMA plasma composition as a function of temperature, at a pressure of 1 bar.

Figure 5. Variation of the 100% PMMA plasma composition as a function of temperature, at a pressure of 1 bar.
Figures 6 to 9 show the equilibrium composition of the Air-PMMA mixture plasma, as a function of the PMMA percentage in the mixture, at thermodynamic equilibrium and at the pressure of 1 bar. These different figures give the variations of the numerical densities of the particles in the plasma of the mixture as a function of the PMMA percentage.

These results show the influence of the PMMA on the plasma composition of the mixture. In each figure, the arrows indicate the increasing direction of the PMMA percentage in the mixture.

From the analysis of all of the curves of Figures 6 to 10, it emerges the following:

1) The numerical densities of neutral diatomic particles C$_2$, H$_2$, CH in the plasma grow with the percentage of PMMA in the mixture while that of the neutral diatomic particles O$_2$, N$_2$, CO, CN, HO and NO decrease.

2) The densities of neutral monoatomic particles C and H in the plasma increase with the rate of PMMA in the mixture while those of neutral monoatomic particles O and N decrease. This can be explained by the evolution of the numerical densities of diatomic particles C$_2$, H$_2$, O$_2$, N$_2$, CO, CN, HO and NO in plasma depending on the PMMA rate.

3) The numerical density of the electrons in the plasma increases as a function of the PMMA percentage in the mixture for temperature values lower than 14000 K. However, for the values of temperatures higher than 14000 K, it tends towards a limit value independently of the PMMA percentage.

4) The numerical densities of the ionized monoatomic particles C$^+$ and H$^+$ increase while those of O$^+$ and N$^+$ decrease in plasma with the PMMA percentage in the mixture. This is linked to the evolution of the numerical densities of particles C, H, O and N in the plasma as a function of the PMMA percentage in the mixture.

5) Double ionized monoatomic particles O$^{2+}$ and N$^{2+}$ have numerical densities that decrease during the numerical density of C$^{2+}$ increases in plasma when the rate of PMMA increases in the mixture.

To show the influence of pressure, we have limited
ourselves to the case of the plasma of the 50% Air -50% PMMA mixture to give the most significant results. The remarks made on the influence of pressure on the composition of this plasma are valid for the other plasmas.

We have reported in Figures 10 to 13, the equilibrium composition of this plasma, for pressures of 1 bar, 2 bar, 5 bar, 8 bar and 10 bar. In each figure, the arrows indicate the increasing direction of pressure.

We note that the numerical densities of neutral monoatomic particles are increasing functions of pressure beyond a value of temperature. Below this temperature value, the numerical densities decrease as the pressure increases. For neutral diatomic particles, their numerical densities increase with pressure.

These remarks can be explained by the following fact: at constant temperature, the number of particles per unit of volume increases when the pressure increases in accordance with the ideal gas equation $P = nkT$. The average energy per particle will therefore decrease. As in plasma, dissociation and ionization reactions are endothermic chemical reactions, they are more difficult to perform for a given temperature when the pressure increases. These reactions therefore take place at higher temperatures the higher the pressure.

There is a marked increase in the numerical densities of the ions $N^+$, $C^+$ and $O^+$ as a function of the pressure above temperatures respectively $T = 17000$ K, $T = 20000$ K and $T = 24000$ K, linked to the decrease in the numerical densities of $N_2^+$, $C_2^+$ and $O_2^+$. We notice that this phenomenon does not concern the ion $H^+$ because there is no ion $H_2^+$.

At very high temperatures, the numerical densities of electrons and $H^+$ tend towards limit values independent of pressure. The shapes of the numerical density curves of $C^+$, $O^+$ and $N^+$ show that we can expect a similar development for pressures above 10 bar. In other words, the numerical densities of these particles will be very low at this same temperature range for very high pressure values.

7. Conclusion

In this article, we have determined the equilibrium composition of plasmas of Air - PMMA mixtures. The
mixedes that are the subject of the study are the mixtures of 80% Air -20% PMMA, 50% Air - 50% PMMA and 20% Air - 80% PMMA. In addition to these mixtures, we also calculated the equilibrium composition of the plasmas of 100% Air and 100% PMMA. The temperature range considered is from 5000 K to 30000 K. The pressure values of 1 bar, 2 bar, 5 bar, 8 bar and 10 bar have been used to show the influence of the pressure on the equilibrium composition plasma. The plasma equilibrium composition is calculated using the thermodynamic equilibrium law of mass action. The results of the calculations clearly show the evolution of the plasma composition in three phases depending on the temperature. The numerical densities of the neutral monatomic particles C and H increase while those of O and N decrease well in the plasma with the percentage of PMMA in the mixture. The numerical density of the electrons in the plasma increases as a function of the percentage of PMMA in the mixture for temperature values below 14000 K. However, for temperature values above 14000 K, it tends towards a limit value independently of the PMMA percentage. For a given temperature, pressure has the main effect of increasing the numerical densities of the particles in the plasma. The increase in pressure leads to a delay in the dissociation and ionization reactions. In other words, these reactions are carried out at higher temperatures when the pressure increases.

Increasing the numerical density of hydrogen in plasma could have advantages in breaking the electrical current in the circuit breaker, but many other plasma parameters should be studied in order to confirm this.

References


