Chemical method for reducing the concentration of electrons in the plasma behind a strong shock wave

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Abstract. In this paper it is shown theoretically using computational methods that the addition of phosphorus-containing substances during the shock wave leads to a decrease in the concentration of electrons at temperatures in the front of shock wave 300 K and behind it of 6000 – 13000° K. Shock wave Mack number is high up to 14. The density is about of 0.35 – 0.7 kg/m³.

1. Introduction

There are various methods for increasing the radio transparency of plasma. The most studied method is based on the injection of water or halocarbon into the stream [1-4]. It is well known that halocarbons are the main destroyer of the ozone layer [5]. In recent work [6] some electron reducing was obtained due to periodically changing of flow regimes. The chemical method seems to be the most preferable for reducing the concentration of the electrons. This method allows to discharge the plasma, whereas the previous methods only increase the mass of charged particles since the plasma frequency also depends on the mass of the charged heavy particles, ions: $\omega_p = \left(\frac{4\pi n e^2}{m_e}\right)^{1/2}$. The decrease in the electron concentration can be used to regulate the operating modes of the plasma torches. The resumption of radio communication during the descent of the spacecraft in the dense layers of the atmosphere is another problem that can be solved.

2. Mechanism

As is known [7,8], the appearance of the electronic component is limited by the process of associative ionization of atomic nitrogen with atomic oxygen up to temperatures of 10,000 K. Associative ionization has a low activation energy of 2.8 eV while the binding energy in a nitrogen molecule (for example) is comparable to the ionization energy of 9.76 eV.

Thus to reduce the concentration of electrons it is necessary to bind atomic nitrogen using a substance that in a molecule with nitrogen has a high binding energy not less than the binding energy of this substance with oxygen and which will not be intensively oxidized as for example carbon. It could be for example arsenic or phosphorus. Preliminary calculations of the equilibrium equations with a constant temperature about 10,000 K showed the possibility of reducing the electron concentration by about an order of magnitude at a sufficiently large molar concentration of injected phosphorus about 0.2.

3. Equations

A one-dimensional system of differential equations of chemical kinetics is calculated together with the conservation equations for the same temperature range (Mach number is about 14). The equations of chemical transformations are taken in the following form:

$$O + N \rightarrow NO^+ + e \quad N_2 + M \rightarrow 2N + M \quad O_2 + M \rightarrow 2O + M$$

$$PN + M \rightarrow P + N + M \quad PO + M \rightarrow P + O + M$$

$$O + NO \rightarrow N + 2O \quad O + N \rightarrow N_2 + NO$$

(1)
The rate constants of the interaction of phosphorus with nitrogen and oxygen were estimated according to the approximate formula given in [7]:

\[
 k_f = N_A \pi \left( r_1 + r_2 \right)^2 \left( 8RT (\pi M_0)^{-1} \right)^{1/2} \cdot \exp \left( -E_A \left( RT \right)^{-1} \right); \quad M_0 = m_1m_2 \left( m_1 + m_2 \right)^{-1},
\]  

(2)

where \(1, 2\) – first and second molecules, \(E_A\) – activation energy, \(r, m\) – radius and mass of molecules.

The velocity behind the shock wave \(V\) and the temperature were calculated using the formulas that are correct for \(M > 5\):

\[
 V = \left( \frac{\gamma - \left( \gamma^2 - 1 \right) \left( \mu E \mu^{-1} + 1 \right)^{0.5}}{\gamma + 1} \right) \cdot \frac{\gamma - \left( \gamma^2 - 1 \right)}{\mu \gamma M^2 \left( \mu_0 \mu^{-1} \left( 1 - V \right) + E \right) / \left( \gamma + 1 \right)},
\]  

(3)

Dimensionless quantities calculated using the formulas

\[
 V = V_\text{dim} / V_0 \quad T = T_\text{dim} / T_0 \quad E = E_\text{dim} \left( \mu_0 V_0^2 / 2 \right)^{-1}. \]

The velocity of the shock wave \(V_0\) and the temperature of the front \(T_0\) were set, and the energy released as a result of chemical reactions \(E_\text{dim}\) was calculated from thermochemical data [9].

The activation energy for diatomic molecules is assumed to be equal to the binding energy in the molecule. It is shown that the temperature change leads to an increase in the electron concentration since the temperature increases due to the association of phosphorus with nitrogen. To reduce the temperature due to dissociation a phosphorus-containing substance such as apatite \(P_2O_5\) was tried but the difficulty was that it contains a lot of oxygen which can increase oxidation and raise the temperature. In addition to estimate the dissociation constant it was difficult to use the approximate formula from [8] since the energy of dissociation activation of a polyatomic molecule can no longer be approximated as the energy of formation of the molecule. Activation energy is estimated as the minimum energy of the beginning of the reaction: half of the formation energy minus two \(PO_2\) formation energies since the apatite molecule is a dumbbell of two \(PO_2\) connected by an oxygen atom. In the calculations the thermochemical data were taken from [9]. Since the mass of \(PO_2\) is large it is this bond that is the weak point in the molecule. So the reaction system is supplemented by the decomposition reaction of \(P_2O_5\) which was taken in simplified form whis reaction constant \(k\):

\[
P_2O_5 + M \rightarrow 2P + 5O + M; \quad k = \pi N_A \cdot 6.25 \cdot 10^{-16} \left( 8 \cdot 8.31 \cdot 10^7 T (24.77\pi)^{1/2} \right)^{0.5} \cdot \exp \left( -3.27 \cdot 10^4 / T \right) P / RT
\]

4. Results

Calculations showed reducing the temperature and a significant decrease in the electron concentration at an acceptable time: up to \(2 \cdot 10^{-4}\) seconds after the shock wave Figure 1.

![Figure 1. Decrease in the electron concentration behind the shock wave at different molar concentration parameter of \(P_2O_5\): 1 – 0; 2 – 0.1; 3 – 0.2; 0 – shock wave position.](image)
$Ce$ is molar fraction of NO$^+$. The molar concentration for all components is the same. It can be seen that when apatite is injected to a molar concentration of 0.2, the concentration of the charged component decreases by almost an order of magnitude. Figure 2 shows the temperature fall behind the shock wave mainly due to dissociation of P$_2$O$_5$.

![Figure 2](image)

**Figure 2.** Decrease in the temperature behind the shock wave at different molar concentration of P$_2$O$_5$: 1 – 0; 2 – 0.1; 3 – 0.2; 0 – shock wave position.

The drop in concentration depends on the drop in temperature but also on the decrease in nitrogen concentration. Figure 3 shows a decrease in the electron concentration due only to a decrease in the nitrogen concentration with addition of P$_2$O$_5$ independent of drop or a rise of temperature. For this purpose the flow was calculated at a constant Mach number then the temperature in both cases will be the same but the shock wave propagation velocities are different.

![Figure 3](image)

**Figure 3.** Decrease in the electron concentration behind the shock wave at different molar concentration parameter of P$_2$O$_5$: 1 – 0; 2 – 0.2. The Mach number is constant $M=14$.

The temperature behind the shock wave is the same 8000 - 13000 K.

Temperature in front of shock wave is 300 K.
The electron concentration decreased by 10%. For practical use it is important to know whether speed preservation matters or temperature preservation. The influence of temperature of course is greater since it is included in the exponent and the dependence on the concentration of nitrogen is power-law. The equilibrium concentration of molecular nitrogen at a constant temperature when P₂O₅ is added also decreases faster: by 14.9% compared to 8.45%.

5. Conclusion
The results show that the proposed mechanism of chemical nature is able to reduce the concentration of electrons at high temperatures by a significant amount at high temperatures by a significant amount: at a constant flow rate - by almost an order of magnitude, and at a constant temperature - by 10%. In the first case, the decomposition of P₂O₅ leads to a decrease in temperature and, thus, to a decrease in the electron concentration by several times. In the second case, nitrogen atoms are bound by phosphorus atoms, and this decrease is 10%. Of course the accuracy of the results of calculating the concentration reduction due to dissociation strongly depends on the method of estimating the decomposition of P₂O₅. The estimate can be improved by using methods for calculating the rate constants of PO₂ separation and then PO₂ decomposition.

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