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Numerical simulation of chemical processes in helium plasmas in atmosphere environment*

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A model is built to study chemical processes in plasmas generated in helium with trace amounts of air at atmospheric pressure or low pressures. The plasma lifetimes and the temporal evolutions of the main charged species are presented. The plasma lifetimes are longer than that in air plasma at atmospheric pressure, but this is not true at low pressures. The electron number density does not strictly obey the exponential damping law in a longer period.

Keywords: helium plasma, chemical processes, lifetime
PACC: 5220, 9410F, 7220J

1. Introduction

Atmospheric discharge has been used extensively in the last decade because of its low cost and convenient operation, as the gas discharge does not need vacuum equipment. Microwave plasma, RF plasma gun, DBD (dielectric barrier discharge) and surface discharge, which have been developed recently, are widely used in fields such as chemical industry, material science, medical attendance and national defence.

Atmospheric discharges usually operate in two regimes. One is the discharge in an open atmosphere environment, near the earth surface or at high altitude. The other is the discharge in closed vessels with air or other gases as the working gas. The former has been studied in our early work,[1] and the latter will be discussed in this paper.

The chemical processes in helium are different from those in pure air. Significantly longer lifetimes of electrons are possible with helium. Helium does not form negative ions, so a major electron attachment mechanism in air is minimized. In a practical laboratory experiment, the filled pure helium in a vacuum vessel will be contaminated by the leakage or wall absorption in the vacuum system. Helium with trace amounts of air is most likely a gas mixture. The contamination of working gas by air components is also inevitable in an open environment. In the ionization process occurring in such a gas mixture, nitrogen and oxygen impurities rapidly form positive ions in charge transfer collisions with helium ions and in turn recombine with electrons and so deionize the helium plasma.

Longer lifetimes of electrons are very useful in some applications, such as plasma radio technology. In these applications electrons would be the primary components, which are useful to absorb or reflect electromagnetic waves and are expected to sustain a high number density.

This work is based on Vidmar's work[2] and our work[1] of numerical simulation in atmospheric plasmas. Vidmar simulated the lifetimes of electrons in helium with air at various altitudes and with different initial electron densities during the ionization process, and calculated the electron lifetime as a function of altitude.[3] But the temporal evolutions of various components were not presented in his papers.

A code has been compiled in the present work, and calculated results are presented for one atmospheric pressure and low pressures in helium with trace amounts of air.

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2. Theoretical model and numerical simulation

The numerical calculation in the present paper is zero-dimensional. It includes ionization, attachment, other physical processes, and main chemical reactions, but ignores spatial processes such as diffusion and flow. As the initial condition, electrons and positive ions with the same number are added into helium with a trace of air at one atmospheric pressure or less. Then the temporal evolutions of various components are monitored during the calculation, some of them belong to the components of natural gas, and some are generated during the chemical reactions. In other words, the process studied is a pulsed ionization with very short ionization reaction period. We do not care about the ionization means (discharge or microwaves) but only focus on the processes after the electron generation.

Initial electrons are generated by the noble gas ionization in our model. The same number densities of positive charge (He^+) are added. The number density of neutral He is the same as that of the total species in natural atmosphere at the same altitude: that is, the pressure in the noble gases is the same as that in air. Trace amounts of air are added into the helium. The proportion of the compositions in the trace air is the same as that in atmosphere at the same altitude.

Thirty-eight species of reactants are considered in our model, as shown in Table 1, including neutral species, positive species (positive ions, hydrated positive ions) and negative species (electron, negative ions, hydrated negative ions), and 229 reactions are considered, including attachment, recombination, deattachment, charge exchange and so on.

Table 1. The main reactants.

Neutral species	Positive species	Negative species
O, O_2, O_3 N, N_2, NO,	O^+, O_2^+, N_2^+, N_4^+, NO^+,	e, O^-, O_2^-, O_3^-, O_4^-,
NO_2, CO_2, H_2O,	H_2O^+, H_3O^+, He^+,	CO_3^-, CO_4^-, $O_2^-\bullet H_2O$,
H, H_2, OH, He,	N^+, He_2^+, $O_2^+\bullet H_2O$,	$CO_3^-\bullet H_2O$,
$He(^3S_1)$	$H_3O^+\bullet OH$, $H_3O^+\bullet H_2O$,	$CO_4^-\bullet H_2O$

In our model the reaction rate equations are as follows:[1]

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = f_i(t, y_1, y_2, \ldots\ldots y_l) \quad i = 1, 2, \cdots 38, \qquad (1)$$

$$f_i = y_i \sum_{j=1}^{38} n_{ij} k_{ij} y_j + y_i \sum_{m=1}^{38} \sum_{j=1}^{38} n_{ijm} k_{ijm} y_j y_m, \quad (2)$$

where y_i denotes the number density of the ith species and f_i is a function involving the rate coefficient for reactions among the ith, jth, and mth species. The terms k_{ij} and k_{ijm} refer to two-body and three-body reaction rates, respectively. The term n_{ij} or n_{ijm} is the integer number of the ith species produced or consumed per reaction event, and is positive if the ith species is produced, and negative if it is consumed.

The Runge–Kutta method[4] is used to solve the constant coefficient nonlinear equations, because the degree of the accuracy of the high-order Runge–Kutta method is very high. Considering the simulating time, we take fourth-order Runge–Kutta method, with high degree of accuracy and short time of simulation.

3. Result of numerical simulation and analysis

3.1. Initial condition and rate coefficient

The chemical processes in helium plasmas in atmosphere environment were numerically simulated at low altitude (near the surface in our model, the pressure is 10^5Pa) and high altitude (at 60km altitude, the pressure is 20Pa, low-pressure plasma). In the simulation at high altitude, some initial conditions, such as the pressure (or the number density of the working gas) and the temperature, are set to be the same as those in the real atmosphere at the same altitude.

Our simulation environment is in helium with trace amounts of air (1ppm in this paper). The initial helium number density is the same as the total number density of all species in air at the selected altitude, $2.5 \times 10^{19}/\mathrm{cm}^3$ near the surface, and $1.0 \times 10^{16}/\mathrm{cm}^3$ at 60km altitude. The initial electron number densities are $1.0 \times 10^{12}/\mathrm{cm}^3$ both near the surface and at 60km altitude, and initial He^+ number densities are the same. The initial number densities of most of the

other neutral species in air are found from some atmospheric chemical papers.[5,6]

Most of the reaction rate coefficients are taken from Refs.[1,5,6]. Some reaction rate coefficients are functions of atmospheric temperature and electron temperature. Atmospheric temperature is set to be 291K near the surface, 253K at 60km altitude,[5] and electron temperature is 2eV, about 23200K. The step length t_0 in our simulation is 10^{-12}s in the first phase of the calculation. As the number density decreases, the step length increases automatically.

3.2. Results and discussion

Figure 1 shows in logarithmic coordinates the temporal evolutions of the number densities of electrons and the total negative charges near the surface. The solid line shows the electron number density, and the dashed line is the total negative charge. As shown in Fig.1, the electron lifetime is 3×10^{-5}s near the surface, the same as Vidmar's.[3] And it is three orders of magnitude longer than the electron lifetime in atmospheric plasmas with air as the working gas near the surface, 1.95×10^{-8}s.[1] The dominant negative species are electrons, and the electron number density is a little less than the total negative charge number density after 1s. The electron number density does not obey the exponential damping law from 10ms to 1s, $10^9/\mathrm{cm}^3$ in 10ms, and $10^7/\mathrm{cm}^3$ in 1s.

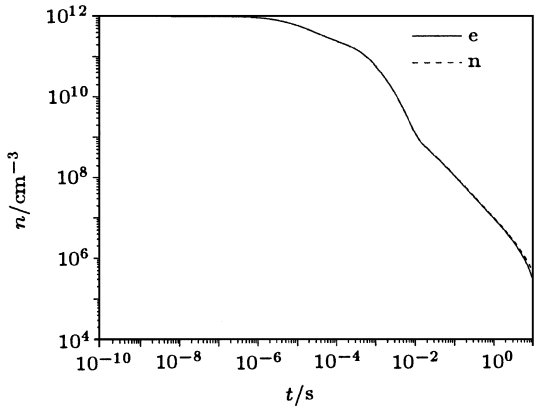


Fig.1. The temporal evolutions of number density n of electron (e) and total negative charges (n) near the surface.

Figure 2 shows the temporal evolution of electron number density at 60km altitude. The electron lifetime at that altitude is almost the same as that near the surface, about 3×10^{-5}s, because dissociative attachment of electrons with ions and three-body electron–electron attachment to positive ions dominate the deionization process in plasmas with high electron number density. This electron lifetime is close to that in the atmospheric plasmas with air as the working gas at 60km altitude, 5.7×10^{-5}s.[1] The electrons do not obey exponential damping law, and can be shown in an inversely proportional to the square root of time in the interval approximately from 10μs to 1s. The trace amounts of air affect the processes greatly at low altitude after a long time, but little at high altitude. In our model, with 1ppm air added into helium, the electron number density becomes less than that in pure helium by about one order of magnitude in 10ms near the surface, and by two orders of magnitude in 0.1s.

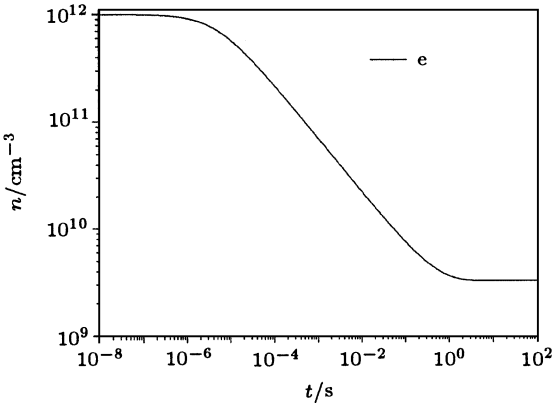


Fig.2. The temporal evolutions of electron number density n at 60km altitude.

As shown in Fig.3, the main negative ions near the surface are oxygen ions O^-, O_2^-, O_3^- and O_4^-, in which O_2^- is the dominant negative ion species throughout the calculation period and increases to a maximum of about $10^8/\mathrm{cm}^3$ in 20μs, while O^- increases to its maximum of $10^6/\mathrm{cm}^3$ in 10ms. Carbon-bearing species increase from the beginning. And the number densities of all negative species are in the range of 10^2–$10^4/\mathrm{cm}^3$ in 10s.

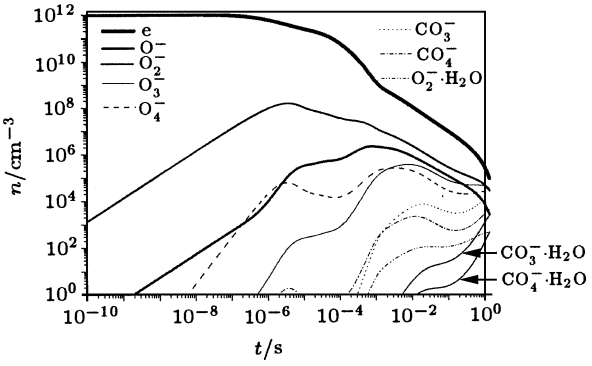


Fig.3. The temporal evolutions of the main negative species near the surface.

Figure 4 shows the temporal evolutions of the main negative ions at 60km altitude. Only O^- and O_2^- exist with the number densities of about 1–100/cm^3 in the time from 1μs to 1s. That means electrons are dominant negative species even throughout the reaction process, and the influence of other negative species can be ignored.

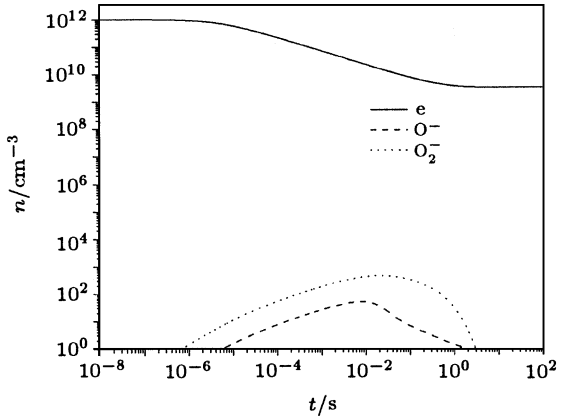


Fig.4. The temporal evolutions of the number density n of the main negative species at 60km altitude.

Figures 5 and 6 show the temporal evolutions of the main positive species. Positive reactions, as shown in the figures, are complex in comparison with the negative reactions. Lifetimes of He^+ are 3×10^{-5}s at the two altitudes. The number density of He^+ obeys exponential damping law near the surface, but does not at 60km altitude, where it can be shown to be inversely-proportional to the square root of time in the interval from 10μs to 1s. As shown in Fig.5, the main positive species except He^+ reach their maxima in 10μs-10ms near the surface. The main positive species devolution is as follows:

$$He^+ \rightarrow N^+ \rightarrow O_2^+ \rightarrow NO^+,$$

NO^+ is dominant after a period of 30ms.

As shown in Fig.6, He^+, N^+, O^+, O_2^+ and N_2^+ are the dominant positive species at 60km altitude. N^+, N_2^+, O^+ and O_2^+ increase first; as the time elapses, the number density of N_2^+ increases to a maximum value of about 3×10^7/cm^3 in 10μs, then decreases slowly until 10ms, and obeys the exponential damping law later. O_2^+ reaches its maximum of about 10^8/cm^3 in 10μs, then decreases following the exponential damping law, while the number density of O^+ increases to 6×10^8/cm^3 in about 10s, and N^+ increases to 3×10^9/cm^3 in about 10s. O^+ and N^+ ions dominate over He^+ after a period of 1s.

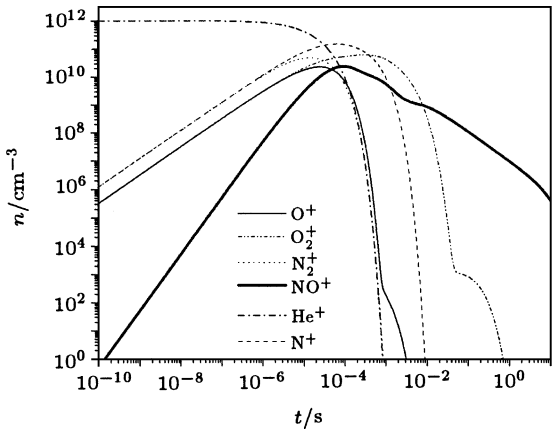


Fig.5. The temporal evolutions of the number density n of the main positive species near the surface.

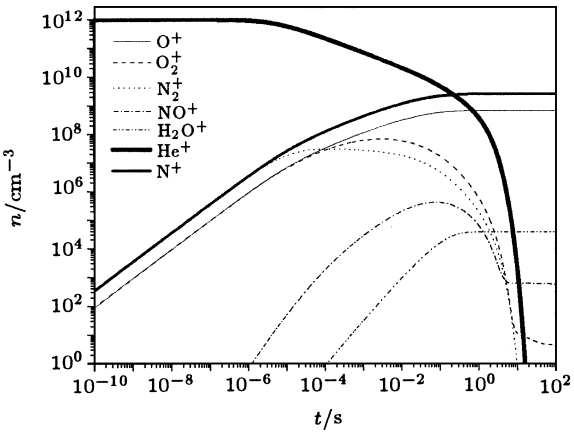


Fig.6. The temporal evolutions of the number density of the main positive species at 60km altitude.

4. Conclusions

A model has been built to simulate the chemical processes in noble gases near the surface (the pressure is 10^5Pa) and at high altitude (60km altitude in this paper, 20Pa). The data of simulation at high altitude are obtained through simulation of homologous low-pressure plasmas. Some results at high altitude are useful in low-pressure plasmas too.

(1) If the initial electron number density is high, the electron lifetime in helium plasma with trace amounts of air does not change with altitude, because dissociative attachment of electrons with ions and three-body electron–electron attachment to positive ions dominate the deionization process in this plasma. The trace amounts of air affect the chemical processes greatly at low altitude after a long time, but little at high altitude. Electrons do not obey the exponential damping law in a long period, and it can be shown to be inversely proportional to the square root

of time in a long period at high altitude. The electron lifetime in helium with trace amounts of air is longer than that in air near the surface of earth, but this is not true at high altitude.

(2) Electron is the dominant negative species in helium with trace amounts of air both at low altitude and at high altitude. The main negative ions are species of oxygen (O^-, O_2^-, O_3^- and O_4^-) at low altitude. Little negative ions exist in the noble gas at high altitude, and the influence of negative ions and hydrated negative ions can be ignored. NO^+ is the dominant positive species at the final stage at low altitude, compared with N^+ at high altitude.

References

[1] Ouyang J M, Guo W, Wang L and Shao F Q 2004 *Chin. Phys.* **13** 2174

[2] Vidmar R J 1990 *SRI Final Report For AFOSR/NP Contract* F49620-85-K0013

[3] Vidmar R J 1990 *IEEE Trans. Plasma Sci.* **18** 4733

[4] Zhang Y H, Xi M Ch and Cheng Ch S 2000 *Numerical Method and Algorithm* (Beijing: Science Press) p153 (in Chinese)

[5] Brasseur G and Solomon S 1984 *Aeronomy of the Middle Atmosphere* (Boston, MA: Reidel)

[6] Heicklen J 1976 *Atmospheric Chemistry* (New York: Academic)