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A Thermodynamic Equilibrium Of Nitrogen Plasma Species Reaction At Atmospheric Pressure: An Application for Afterglow

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Abstract

Before producing nitrogen plasma at atmospheric pressure in experiment, a simulation is carried out to show the equilibrium processes by chemical kinetic reaction. Nitrogen species density is guided by continuity equation where chemical processes and Arrhenius form are used to follow the change of density over the time. Those formula are integrated to obtain density and the reaction rate of each reaction.

This result show that the equilibrium can be reached and generally agree with the Saha Boltzmann calculation. An afterglow application is also shown in this model where the electron is dominant in collision and cooling time is in millisecond.

Keywords
Afterglow, Chemical Reaction, Nitrogen Plasma, Simulation.

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1. Introduction

The ratios of nitrogen plasmas species in atmospheric pressure plasmas depend on the temperature. Species interact with each other mainly by binary and ternary collision. In order to calculate the species densities to reach thermodynamic equilibrium under various conditions, a simple chemical kinetic reaction has been simulated. This is approached through the nitrogen reaction processes is zero-dimensional and time dependent. It solves the rate equations for a set of interacting species, given their initial densities and temperatures, with the latter held constant.

2. Chemical Kinetic Reaction

To describe a chemical kinetic reaction, we use the continuity equation for each species, i.e.,

$$\partial n_i / \partial t + \nabla . (n_i v_i) = S_i$$

where n_i is density, v_i is velocity depending on position, and S_i is the particle source per unit volume, per unit time for ith species. The diffusion effect is ignored due to the high collision rate of particles at atmospheric pressure resulting in long time scale for diffusive losses compared with a relatively short time scale to achieve local equilibrium. Therefore the equation becomes 0-D(zero dimensional) and time dependent, i.e.,

$$dn_i/dt = S_i$$

This equation implies that a change of density is entirely due to the source term, S_i. No energy balance equation is used and the temperature of species is imposed. The source term depends on the various reactions, in which the species considered takes part, hence $S_i = \Sigma_{j=1}^{N} S_{ij}$ where S_{ij} is rate of production of species *i* in reaction *j*. S_{ij} is calculated by multiplying the reaction rate, R_j by the number of molecules of the species produced (or destroyed) in the reaction. In a reaction process represented by

$$aA + bB \quad cC + dD + ...,$$

$$R_{fj} = k_{fj} [A]^a [B]^b, \quad Rrj = k_{rj} [C]^c [D]^d ...,$$

represent reaction rates for forward and reverse reaction, respectively.

The Arrhenius form is used to describe the rate constants (k_j) as a function of temperature

$$<kj>=\acute{a}_j (T_{(reaction)} / 300)^{\hat{a}j} \exp(-\bar{a}_{j/} T_{(reaction)})$$

The rate constant at a given temperature allows the reaction rate to be calculated if species densities are given.

The total source of ith species for all reactions is: $dn_i/dt_{(react)} = \Sigma_{(j=1)}^{N} (M\{r_{ij}\} - N\{f_{ij}\})(R\{f_j\} - R\{r_j\})$
where $M\{r_{ij}\}$ and $N\{f_{ij}\}$ are the number of molecules of ith species in reaction j for products and reactants, respectively. Since the density of each species changes over the time, the total pressure will change as given by the sum of the partial pressures of the plasma species i.e., $p = {}_{(l=1)}^{N} n_l kT_l$. When total pressure is not constant hence $1/p\ dp/dt = 1/\hat{o}$, where $\hat{o}$ is the time. Finally we combine two terms of equation for ith species obtained

$$dni/dt_{(correction)} = dn_i/dt_{(react)} - n_i/p\ dp/dt$$
$$= dn_i/dt_{(react)} - ni\ \Sigma_{(l=1)}^{N} T_l (dn_l/dt)\{T_l n_l\} \text{.........}(1)$$

3. Integration of The Rate Equations

Nitrogen plasmas have several kinds of chemical species as shown in table 1. To integrate equation (1), we use the MATLAB 5 program, Ode45. The input numbers are initial densities (n_o) for 6 species of the order 10^{10} m^{-3} to 10^{25} m^{-3} however, for quasineutrality, the initial density for electrons (n_e) and ion species ($n_{(ion)}$) must be the same.

Tabel 1. Nitrogen Reaction Composition With Arrhenius Parameters

No.	Reaction	α	β	γ	Reference
1(maju)	$e^- + N_2 \rightarrow e^- + e^- + N_2^+$	2.4×10^{-15}	0.5	168200	Reaksi 2
1(reward)		0	0	0	Not available
2(forward)	$e^- + N \rightarrow e^- + e^- + N^+$	2.4×10^{-15}	0.5	168299	(Bell, 1982)
2(reward)		0	0	0	Not available
3(forward)	$2N_2 + N_2^+ \rightarrow N_2 + N_4^+$	6.0×10^{-41}	-1.85	0	(Rowe,1984)
3(reward)		0	0	0	Not available
4(forward)	$e. + N_2^+ \leftrightarrow N + N$	1.8×10^{-13}	0.39	0	(Mitchel,1990)
4(reward)		3.8×10^{-19}	1.5	67500	(Domingo, 1995)
5(forward)	$N_2 + N + N \leftrightarrow N_2 + N_2$	6.9x10-44	1.6	0	(Bauch,1973)
5(reward)		6.7×10^{-13}	-1.6	113200	(Bauch, 1973)
6(forward)	$N + N_2^+ \leftrightarrow N_2 + N^+$	1.0×10^{-17}	0	0	Not available
6(reward)		2.9×10^{-17}	0.5	12200	(Domingo, 1995)
7(forward)	$e^- + N^+ \rightarrow N$	3.8×10^{-18}	-0.62	0	(3210,Base)
7(reward)		0	0	0	Not available
8(forward)	$e^- + N_4^+ \leftrightarrow N_2 + N_2$	1.4x10-12	0.41	0	(Mitchel,1990)
8(reward balik)		1.0×10^{-17}	0	168200	(Guera,1997)
9(forward)	$N2 + N \leftrightarrow N + N + N$	9.6×10^{-12}	1.5	113200	(Domingo, 1995)
9(reward)		2.9×10^{-43}	-1.6	0	(Bauch,1973)
10(forward)	$e^- + N_2 \rightarrow e^- + N + N$	5.4×10^{-10}	1.6	113200	(Domingo, 1995)
10(reward)		0	0	0	Not available

4. Result and Discussion

Thermal Plasma

Figure (1) shows a comparison of results of [1] shown by lines and code results shown by dots. The code results are obtained where the temperature of all species is put equal. The solution goes to convergence where the density changes will go to zero by tolerance number 10^{-3}. The initial density does not change equilibrium state. It is not surprising when a species density is dominant, that the code results agree because the species partial pressure is nearly atmospheric, such as N and N_2 at 6000K. When the temperature increases, most reaction rates increase. Implicitely, when the temperature is higher, the time to reach equilibrium is shorter. The forward and reverse rates of some reactions are balanced at 6000, 8000, 10000, 12000 and 14000K. The following is the thermodynamic equilibrium for nitrogen reaction (e.g, 10000K).

Reaction Rate ($m^{-3}s^{-1}$)

(forward)	(reward reaction)			
5.731e+021	0.000e+000	$e + N_2$	=	$N_2^+ + e + e$
5.951e+024	0.000e+000	$e + N$	=	$N+ + e + e$
3.055e+018	0.000e+000	$N_2^+ + N_2 + N_2$	=	$N_2 + N_4^+$
4.179e+028	4.191e+028	$e + N_2^+$	=	$N + N$
8.307e+022	1.350e+022	$N_2 + N + N$	=	$N_2 + N_2$
5.157e+026	3.977e+026	$N + N_2^+$	=	$N_2 + N^+$
6.378e+025	0.000e+000	$e + N^+$	=	N
3.280e+018	2.254e+017	$e + N_4^+$	=	$N_2 + N_2$
2.853e+026	3.625e+026	$N_2 + N$	=	$N + N + N$
1.997e+026	0.000e+000	$e + N_2$	=	$e + N + N$

Figure 1: Validation of simulation result (dot) compared to Saha Boltzmann (line).

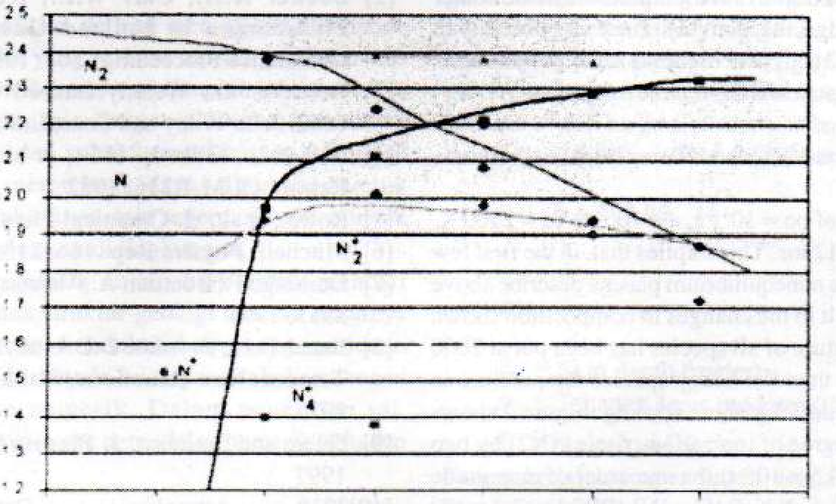

Figure 1

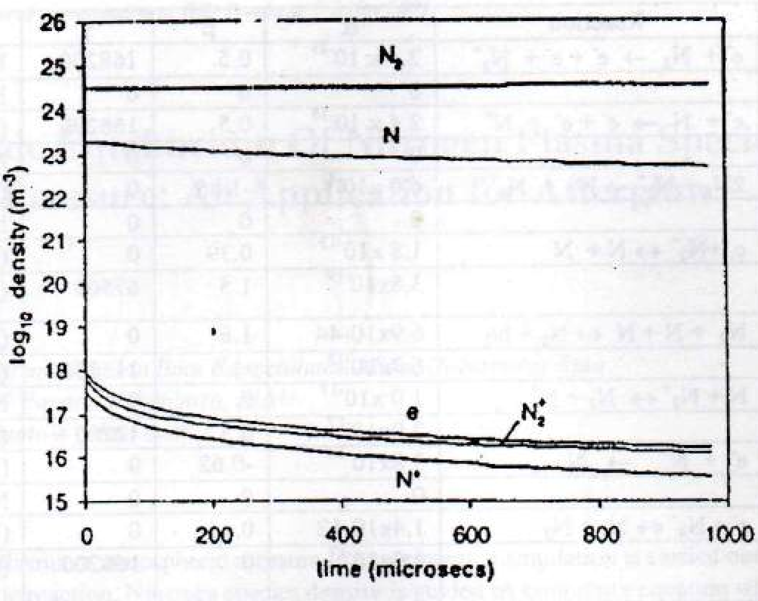

Figure 2

Application in Afterglow
In the case of power input is removed, the characteristic electron energy decline rapidly and the electron are thermalised. The electron energy loss rate due to collision with heavy particles is much less than the momentum loss rate. Nevertheless, we calculate that the electron will thermalize with the heavy particles in a few ns. Thus we expect that all species in the afterglow will have the same temperature, though initially the composition is far from the equilibirum.

The time scale for cooling by thermal conduction depends on the plasma size and shape and on the thermal conductivity and its temperature dependence. It is given approximately by the ratio W/P, where P is the power input required to sustain an energy content W in the steady-state. Taking a cylindrical plasma of a radius a, which could represent a stream of process gas emerging from a source, and a thermal conductivity of the form $\hat{e} = AT$ (which is good approximation for temperature up to 4000K with $A = 5 \times 10^{-5}\ W\ m^{-1}\ K^{-2}$ [11]). It is straightforward to show that the power per unit volume required for sustainment is $4A(To^2 - Ta^2)/a^2$, where To and Ta are temperature in the center of the cylinder and the edge, respectively. The energy density in the cylinder is at least 3/2 (po), where the po is the gas pressure, so the colling time is approximately

$$\tau_{cool} = (3\ po\ a^2)/\ ([\ 8\ A\ (To^2 - Ta^2)]$$

Inserting typical values of $po = 10^5$ Pa, $a = 10^{-2}$ m, To = 2500 K, Ta=300 K gives $\tau_{cool} = 12$ ms. This implies that, in the first few ms of the afterglow of the nonequilibrium plasma describe above for a period of 1 ms result in the changes in composition shown in figure 2. The temperature of all species has been put at 2000 K, i.e. somewhat lower than the heavy species temperature in the source, 2320 K, to allow for some cooling. Figure 2 shows a rapid decline in the degree of ionization,, *fi* =(e)/(N2) by two orders of magnitude to 4.5×10^{-9} and a one order of magnitude decrease in the degree dissociation, *f*d = [N] / 2[N_2] to 7.2×10^{-3}

5. Conclusion and Suggestion

The simulation shows generally good agreement with Saha Boltzmann calculation except that at temperatures above 10000K, the density of N_2 given by the code decreases faster than expected. The model indicates that the main species is atomic nitrogen produced by electron dissociation of molecules. This reaction absorbs a large fraction of the power input to electron from the electromagnetic field. Recombination in the afterglow by three body collisions with molecules results in an order of magnitude decrease in the density of atomic nitrogen in a time of 1ms.

Spectroscopic measurements are underway to check these predictions and will be reported in a future paper. Also, this model can be developed for time and dimensions dependence where diffusion effect is involved.

6. References

[1] Veprek S., Venugopolan M., editors. High Pressure Plasmas and their Application to Ceramic Technology., **Topic in Current Chemistry 107, Plasma Chemistry IV**. Springer-Verlag, Berlin Heidelberg,1983

[2] Becker K.H., Carr W.E., Kunhardt E.E., editors. **Phenomena in Ionized Gases**, XXII ICPIG, AIP Conference Proceedings 363, 1995

[3] Delcroix J.L., **Weakly Ionised Gases, Plasma Physics**, vol.2. John Wiley and Sons, Ltd., 1966

[4] Bell K.L., Gilbody H.B., et al., **Culham Laboratory Report CLM-R216**, 1982

[5] Rowe., et al., **J. Chemical Physics**, 80, 4915, 1984

[6] Mitchell, **Physics Rep.**,186, 215, 1990

[7] Domingo P., Bourdan A., Vervisch P., **Physics Plasmas,** 2, 2853, 1995

[8] Bauch D.L., Drysdale D.D. et al., **Evaluated Data for High Temperature Reactions**, Vol.2, Butterworth's London, 1973

[9] Guera and Loureiro, **J. Plasma Sources Sci.Tech.6**, 361, 1997

[10]3210 Astrophysics Database, http://saturn.phy.umist.ac.uk:8000/~tjm/rate/rate.html

[11] Murphy A B and Arundel C J 1994 Plasma Chem. Plasma Process. 14 451