

Thermodynamic Equilibrium of Nitrogen Species Discharge: Comparison with Global Model

Saktioto, F.D Ismail, P.P. Yupapin, J. Ali

Abstract—The equilibrium process of plasma nitrogen species by chemical kinetic reactions along various pressures is successfully investigated. The equilibrium process is required in industrial application to obtain the stable condition when heating up the material for having homogenous reaction. Nitrogen species densities is modeled by a continuity equation and extended Arrhenius form. These equations are used to integrate the change of density over the time. The integration is to acquire density and the reaction rate of each reaction where temperature and time dependence are imposed. A comparison is made with global model within pressure range of 1-100mTorr and the temperature of electron is set to be higher than other nitrogen species. The results shows that the chemical kinetic model only agrees for high pressure because of no power imposed; while the global model considers the external power along the pressure range then the electron and nitrogen species give highly quantity densities by factor of 3 to 5.

Keywords—chemical kinetic model, Arrhenius equation, nitrogen plasma, low pressure discharge

I. INTRODUCTION

NITROGEN plasmas have been studied for many years, because these plasma discharges create a high density of nitrogen atoms that may be used for materials processing. Furthermore, there is interest in nitrogen plasmas that operate at atmospheric pressure, since they offer several advantages over their low-pressure counterparts [1]. Low-pressure plasmas have a dominant and long-established role in processing of materials ranging from silicon wafers to magnetic storage disks and thin film coatings. This is because the unmatched capability of low pressure plasma devices in providing a vast array of chemically active species, selectable

Saktioto is with the University of Riau, Pekanbaru, Indonesia and associated with Advanced Photonics Science Institute, University Technology Malaysia, 81310, UTM Skudai, Johor, Malaysia. (corresponding author phone: +60167630212 fax: +6075566162, -mail: saktioto@yahoo.com)

F. D. Ismail is with the Advanced Photonics Science Institute, University Technology Malaysia, 81310, UTM Skudai, Johor, Malaysia (e-mail: fairuzdiyana@fs.utm.my)

P.P. Yupapin is with the Faculty of Science, King Mongkut's Institute of Technology Ladkrabang Bangkok 10520, Thailand (e-mail: kypreech@kmitl.ac.th).

J. Ali is with the Advanced Photonics Science Institute, University Technology Malaysia, 81310, UTM Skudai, Johor, Malaysia. (e-mail: jalil@bip.utm.my)

ion flux, low gas temperature, and high uniform reaction rate over a relatively large area [2].

However, in principle, atmospheric pressure plasma devices can be a crucial advantage over low pressure plasmas because they eliminate complications introduced by the need for vacuum. For example, atmospheric pressure discharges have been used for a number of applications such as high temperature materials processing and ozone production for water purification. Nowadays, otherwise, the use of atmospheric pressure discharges for materials applications has not been widely realized, compared to low pressure plasmas. This is because of the high gas temperature in the discharge, or the limited production of chemically active species due to localization of the discharge [2].

There is considerable interest in methods for efficiently producing large volume of atmospheric pressure air plasmas with free electron densities $\sim 10^{13} \text{ cm}^{-3}$ at gas temperatures between 300 and 2000K [3]. It is important to understand the chemical mechanism of dissociation, ionization, and recombination in air and nitrogen plasmas, with kinetic temperature of the free electrons (T_e) being higher than the kinetic temperature of heavy species (T_g). The most distinct feature that distinguishes non-equilibrium discharge plasmas from other discharge plasmas is the electron temperature (T_e), i.e. average electron energy in the plasmas is about two orders of magnitude higher than ion temperature (T_i) and neutral or gas temperature (T_g) [4]. Such plasmas are sometimes referred to as two-temperature plasmas. Therefore, the investigation of nitrogen plasma species in a wide range pressure from low to higher pressure is interesting phenomena for obtaining the equilibrium state when the nitrogen species breakdown.

In order to calculate the species densities to reach thermodynamic equilibrium under various conditions, a simple chemical kinetic reaction has been simulated. It solves the rate equations for a set of interacting species. It will then discuss the application model to low pressure discharge. In this work, we will further investigate the behavior of nitrogen species densities at given initial pressure, densities and temperature. The comparison with steady state model is analyzed and a global model is applied to study the low pressure of nitrogen discharge.

In order to investigate the equilibrium state a set of reaction set of nitrogen plasma is introduced. The rate of reaction is calculated to investigate how fast a reaction process occurs. The concept of rate coefficient is used in a similar fashion to describe reactive collisions between the randomly moving heavy particles, where the reaction probability is determined by the relative velocity between the colliding heavy particles.

At equilibrium conditions, the temperature dependence of the rate coefficient can be described by an Arrhenius equation [5].

This paper is intended to achieve the equilibrium state for various pressure conditions by obtaining the proper temperature. The chemical kinetic reaction of nitrogen species and the comparison with a global model are also depicted. The most dominant reaction rates are not only required to demonstrate the thermodynamic equilibrium process but also to determine significant species densities in contributing the combustion process of the material. In this purpose, five nitrogen species; N_2 , N_2^+ , N , N^+ , N_4^+ and electron are chosen. The integration of chemical kinetic model and the reaction rates for low pressure discharge are investigated.

II. THEORETICAL CONSIDERATION

A. Chemical Kinetic Model

To describe a chemical kinetic reaction, we use the continuity equation [7] for each species, i.e

$$\partial n_i / \partial t + \nabla \cdot (n_i v_i) = S_i \quad (1)$$

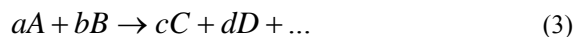
where n_i is density, v_i is velocity depending on position, and S_i is the particle source per unit volume, per unit time for i^{th} species. For atmospheric pressure plasmas, as noted above, we

neglect the diffusive term $\nabla \cdot (n_i v_i)$ in equation (1) [3].

Therefore the equation becomes 0-D (zero dimensional) and time dependent, i.e.,

$$dn_i / dt = S_i \quad (2)$$

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 $S_i = \sum_{j=1}^N S_{ij}$ where S_{ij} is rate of production of species i in reaction j . S_{ij} is calculated by multiplying the reaction rate, R by the number of molecules of the species produced (or destroyed) in the reaction. In a reaction process represented by



represents reaction rates for forward and reverse reaction.

The Arrhenius form is used to describe the rate constants (k) as of a reaction on the absolute temperature

$$k = \alpha(T/300)^\beta \exp(-\gamma/T) \quad (4)$$

where T is the reaction temperature in K. The rate constant at a given temperature allows the reaction rate to be calculated if

species densities are given. The species included in the chemical kinetic model are electrons, N_2 , N , N^+ , N_2^+ and N_4 . The equations are integrated using the MATLAB routine ode45 from the given initial values of n_i . The initial values are constrained to satisfy charge neutrality, i.e if Z_i is the charge on the i^{th} species, n_i , is regarded as vector, is adjusted to be orthogonal to Z_i .

The total source of i^{th} species for all reactions is:

$$dn_i / dt_{(react)} = \sum_{j=1}^N (M\{r_{ij}\} - N\{f_{ij}\})(R\{f_{ij}\} - R\{r_{ij}\}) \quad (5)$$

where $M\{r_{ij}\}$ and $N\{f_{ij}\}$ are the number of molecules of i^{th} species in reaction j for products and reactants, respectively. Since the density for 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. $p = \sum_{i=1}^N n_i k T_i$. When the

total pressure is not constant hence $1/p dp/dt = 1/\tau$, where τ is the time. Finally we combine two terms of equation for i^{th} species obtained

$$\begin{aligned} dn_i / dt_{(correction)} &= dn_i / dt_{(react)} - (n_i / p)(dp/dt) \\ &= dn_i / dt_{(react)} - n_i \sum_{j=1}^N T_j (dn_j / dt) \{T_j n_j\} \end{aligned} \quad (6)$$

Table 1 shows the chemical reactions of nitrogen plasma species. Some values of Arrhenius constants are shown by references and others are not available. These reactions are considered to be dominant collisions to achieve thermodynamic equilibrium. The equilibrium state is shown by collisions of nitrogen species for forward and reverse reactions are balance subject to reaction rate of Arrhenius form.

B. A global model for steady state condition.

Plasma discharged is assumed to be quasi-neutral [10]. Plasma distribution in chamber makes distribution electrons, ions and slightly atoms or molecules depending in pressure, temperature and densities. Plasma species collide with particles and the boundary of chamber. Some particles collides produces new particles and other destruct particles. These processes depend on time and the geometry of plasma boundary.

The movement of particles for instance is affected by diffusion, electron static and photon and mechanical effect of particles. In the global model calculation, a particular electron distribution function for the discharge, the simplest using the Maxwellian-like distribution such as temperature and density of electron energy distribution. The Maxwellian & Druyvesteyn distributions is as follows

$$f(\epsilon) = c_1 \epsilon^{1/2} \exp(-c_2 \epsilon^x) \quad (7)$$

TABLE I NITROGEN REACTION COMPOSITION WITH ARRHENIUS PARAMETERS [7]

No	Reaction	α	β	γ	Reference
1(forward)	$e^- + N_2 \rightarrow e^- + e^- + N_2^+$	2.4×10^{-15}	0.5	168200	Reaction 2
1 (reverse)		0	0	0	Not available
2 (forward)	$e^- + N \rightarrow e^- + e^- + N^+$	2.4×10^{-15}	0.5	168299	(4)
2(reverse)		0	0	0	Not available
3(forward)	$2N_2 + N_2^- \rightarrow N_2 + N_4^+$	6.0×10^{-41}	-1.85	0	(5)
3(reverse)		0	0	0	Not available
4(forward)	$e^- + N_2^+ \leftrightarrow N + N$	1.8×10^{-13}	0.39	0	(6)
4(reverse)		3.8×10^{-19}	1.5	67500	(7)
5 (forward)	$N_2 + N + N \leftrightarrow N_2 + N_2$	6.9×10^{-44}	1.6	0	(8)
5 (reverse)		6.7×10^{-13}	-1.6	113200	(8)
6 (forward)	$N + N_2^+ \leftrightarrow N_2 + N^+$	1.0×10^{-17}	0	0	Not available
6 (reverse)		2.9×10^{-17}	0.5	12200	(7)
7 (forward)	$e^- + N^+ \rightarrow N$	3.8×10^{-18}	-0.62	0	(9)
7 (reverse)		0	0	0	Not available
8 (forward)	$e^- + N_4^+ \leftrightarrow N_2 + N_2$	1.4×10^{-12}	0.41	0	(6)
8 (reverse)		1.0×10^{-17}	0	168200	(10)
9 (forward)	$N_2 + N \leftrightarrow N + N + N$	9.6×10^{-12}	1.5	113200	(7)
9 (reverse)		2.9×10^{-43}	-1.6	0	(8)
10(forward)	$e^- + N_2 \rightarrow e^- + N + N$	5.4×10^{-10}	1.6	113200	(7)
10(reverse)		0	0	0	Not available

where $x = 1$ corresponds to the Maxwellian distribution and the $x = 2$ to the Druyvesteyn distribution. c_1 and c_2 are coefficients which depend on the energy ε and the distribution parameter x . In term of energy distribution function, the function of particles, such as electron can be fit the result, to the Arrhenius form.

The main idea of a global model is to neglect the complexity which arises when spatial variations are considered and to generate a model that encompasses large number of reactions in order to model processing plasma with a limit computing number. Here, the global model of nitrogen plasma discharge is developed for the pressure regime 1-100mTorr. A reaction rate is created and the reaction rate coefficient reviewed and evaluated [10]. In addition to electrons, the nitrogen discharge consists of molecular nitrogen N_2 , atomic nitrogen N , and the positive ions N_2^+ , N^+ , N_4^+ , N_3^+ . A comprehensive reaction set has been developed that includes roughly 450 interactions of the discharge species. Electrons are assumed to have a Maxwellian-like energy distribution in the range of 1-10 V [6].

Other parameters are normally simplified for global model is electron velocity distribution function at the boundary condition

$$c_2 = \frac{1}{\langle \varepsilon \rangle^x} \left[\frac{\Gamma(\xi_2)}{\Gamma(\xi_1)} \right]^x \quad (8)$$

where $\langle \varepsilon \rangle$ is the average electron energy, $\Gamma(\xi)$ is the solution to the gamma function with $\xi_1 = 3/2 x$ and $\xi_2 = 5/2x$. The sheath potential, V_s is given by

$$V_s = -T_e \ln \left(4 \frac{n_i u_B}{n_e v_e} \right) \quad (9)$$

where energy distribution is kinetic energy, T_e is electron temperature, n_i is ion density, n_e is electron density, v is average electron velocity.

Consideration of collision energy loss per ionization event is significant of total power loss due to collision of particle, elastic and inelastic collision including all rotational, vibrational and electronic excitation, dissociation, attachment and detachment process. Detailing balancing of model consider momentum conservation of particles, describing kinetic energy and total energy. Maxwellian averaged inverse reaction rate in consistent size the principle of detailed balancing. Systems of equations consist of particle balance, volume losses, and all losses at the wall including pumping losses. Particle balance equation and are found

$$\frac{dn^{(\alpha)}}{dt} = \left[\sum_{\beta G} R_{r,\beta G}^{(\alpha)} + R_{iw,G}^{(\alpha)} + R_{mw,G}^{(\alpha)} + R_{Qi}^{(\alpha)} + R_{rad,G}^{(\alpha)} \right] - \left[\sum_{\beta L} R_{r,\beta L}^{(\alpha)} + R_{iw,L}^{(\alpha)} + R_{Q0}^{(\alpha)} + R_{rad,L}^{(\alpha)} \right] \quad (10)$$

Where $\frac{dn^{(\alpha)}}{dt}$ is particle balance equation for a discharge species α , $R_{r,\beta G}^{(\alpha)}$ is the generation of a species α , $R_{iw,G}^{(\alpha)}$ is the generation of a species α (A^+ or A), respectively, $R_{mw,G}^{(\alpha)}$ is the generation of a species α (B or B_2), $R_{Qi}^{(\alpha)}$ is the rate due to the flow of a species α into a chamber of volume V , $R_{rad,G}^{(\alpha)}$ is the generation of a species α (A^* or A), $R_{r,\beta L}^{(\alpha)}$ is the loss of a species α , $R_{iw,L}^{(\alpha)}$ is the loss of a species α (A^+ or A), $R_{mw,L}^{(\alpha)}$ is the loss of a species α (B or B_2), $R_{Qo}^{(\alpha)}$ is the rate due to the flow of a species α out of a chamber of volume V and $R_{rad,L}^{(\alpha)}$ is the loss of a species α (A^* or A).

They are used for a discharge in the steady state the plasma parameters. Furthermore, the global model is applied to investigate the reaction rates for the creation and loss of the discharge species as a function of discharge pressure. We highlighted the comparison of electron and electron temperature density which measured by Singh and Graves[10].

III. INTEGRATION AND APPLICATION MODEL TO LOW PRESSURE DISCHARGE

The integration of kinetic model from low to high pressure discharge is implied by setting the initial values of densities, pressure and temperature species [10]. These reactions are evaluated to reach equilibrium. These results are shown on Figure 1.

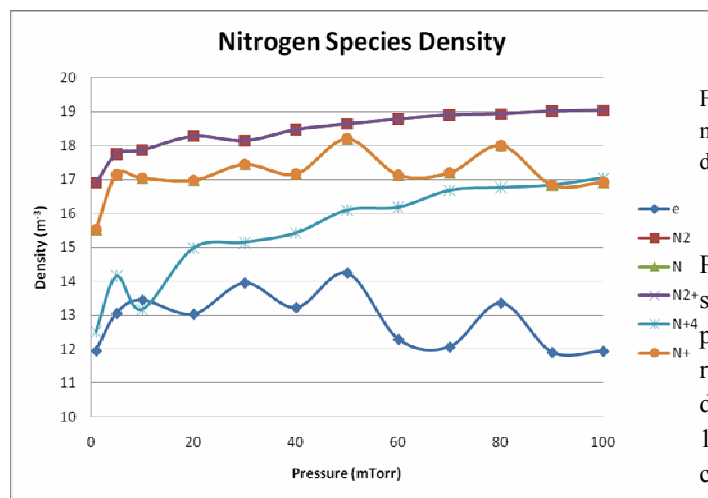


Fig. 1 Nitrogen species density for $T = 1.8\text{eV}$ to 7eV

Twelve points at different pressure is selected; 1-100mTorr respectively. N_2 and N densities are considered to be equivalent with N_2^+ and N^+ . For high pressure (80-100mTorr), the integration of nitrogen species density agrees to Saha Boltzmann condition [7]. The initial electron number density increase occurs by electron-impact ionization process. Along increasing pressure, the reaction rate of electron is almost stable and varies between $10^{10}\text{m}^2\text{s}^{-1}$ to $10^{12}\text{m}^2\text{s}^{-1}$. Atomic nitrogen, N starts with reaction rate at $10^6\text{m}^2\text{s}^{-1}$ for pressure 1mTorr, but as the pressure increases to 50mTorr, the reaction increase up to $10^{12}\text{m}^2\text{s}^{-1}$. From the 60mTorr to 100mTorr, the reaction rate for N is slightly fluctuated over the densities until it reaches $10^9\text{m}^2\text{s}^{-1}$ at pressure 100mTorr. The most stable and highest reaction rate among all five species is N_2 . Along the increasing pressure, the reaction rate reach the highest at few pressure points with reaction rate is $10^{20}\text{m}^2\text{s}^{-1}$. As we look further to the reaction rate, N_2 is the most produced species. This agrees with the result generated on N_2 density in Figure 1. N_4^+ behavior of reaction rate is almost constant along the increasing pressure. This contradicts with its density in Figure 1. Other two species, N_2^+ and N^+ , the reaction rate is comparable with N_2 and N .

IV. COMPARATIVE MODEL

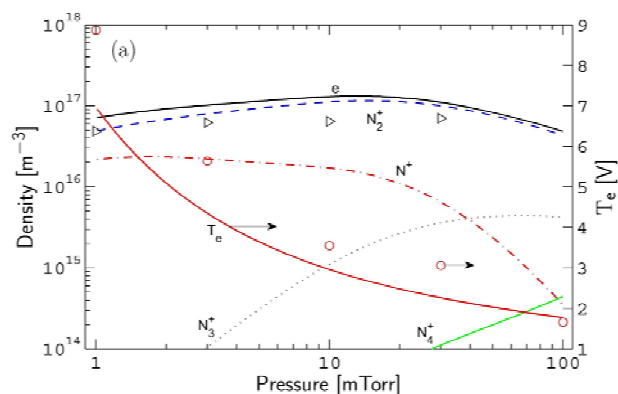


Fig. 2 The electron density and the electron temperature in global model measured by Singh and Graves (2000b) as a function of discharge pressure [6]

Figure 1 is generated using initial values from Figure 2. Points at each respective pressure from 1-100mTorr are selected. Electron and N_2^+ density is almost constant along the pressure. While N^+ species had slight drop after the pressure reach 20mTorr. The density of N^+ is comparable to the N_2^+ density at 1mTorr, but decreases rapidly with pressure above 10mTorr. For N_4^+ , the density agrees with increasing linear curve and appears at 30mTorr. Therefore, we conclude that the discharge of nitrogen species is essentially atomic at low pressure but is dominated by molecular nitrogen at high pressure [6]. As we compare Figure 1 to Figure 2, the trend

curve is almost identical for N_2 and N_2^+ . The electron number density as a function of electron temperature presents the mechanisms governing ionization and electron recombination in discharges.

There are few parameters should be taken into consideration while discussing this comparison. While in chemical kinetic model, temperature dependence is modeled through species density and can increase up to 14000K. This can cause major difference to our result especially at electron density versus pressure. For chemical kinetic model, no photon is required and no power or external source is involved. There is also energy in type of absorbed power injected to global model. In global model, the lower temperature is assumed to have linear dependence on the absorbed power, $T_g = 0.17 \times P_{abs} + 387K$.

V. CONCLUSION

Chemical kinetic model has been investigated from pressure range 1-100mTorr. This model is also applied and compared to the global model. It shows the kinetic model does not agree with global model of species densities by factor of 3 to 5. The external power is not imposed, where global model generates nitrogen plasma by absorbed power in the range of 240-500 W. This power will affect photon and temperature variation along the internal collisions. However, the chemical kinetic model agrees for equilibrium state showing the species densities where electron and other temperature species are set equal to high pressure. Re-correction of chemical kinetic model is underway and required by imposing power source and variation of pressure while photon in chemical reaction is considered.

ACKNOWLEDGMENT

We would like to thank the Institute of Advanced Photonic Science, Enabling Science & Nanotechnology (ESciNano) Research Alliance, Universiti Teknologi Malaysia (UTM) and University of Riau, Indonesia for generous support in this research.

REFERENCES

- [1] S. E. Babayan, G. Ding and R. F. Hicks, "Determination of the nitrogen atom density in the afterglow of a nitrogen and helium, nonequilibrium, atmospheric pressure plasma," *Plasma Chemistry and Plasma Processing*, 21(4)(2001) 505-521
- [2] J. Park, I. Henins, H. W. Herrmann, and G. S. Selwyn, "An atmospheric pressure plasma source," *Appl. Phys. Lett.*, 76(3)(2000) 288-290
- [3] L. Yu, Laurent Pierrot, Christophe O. Laux, Charles H. Kruger, "Effects of vibrational nonequilibrium on the chemistry of two-temperature nitrogen plasmas," *Plasma Chemistry and Plasma Processing*, 21(4)(2001) 483-503
- [4] Toshiki Nakano, "Some recent topics of non-equilibrium discharge plasma technologies," *IEEE Trans. on Dielectrics and Electrical Insulation*, 14(5)(2007)1081-1087

- [5] K.H Becker, U. Kogelschatz, K.H Schoenbach, R.J Barker, "Non-equilibrium air plasmas at atmospheric pressure, IoP Publishing, 2004, page 125-126.
- [6] E. G. Thorsteinsson and J. T. Gudmundsson, A global (volume averaged) model of the nitrogen discharge: I. Steady State, *Plasma Sources Science and Technology*, 18 (4) (2009) 045001
- [7] J Hugill, T Saktioto, A simplified chemical kinetic model for slightly ionized, atmospheric pressure nitrogen plasmas, *Plasma Sources Science and Technology*, 10 (38) (2001) 38-42
- [8] Saktioto, A thermodynamic equilibrium of nitrogen plasma species at atmospheric pressure: An application for afterglow, *Kontribusi Fisika Indonesia*, 13(2)(2002) 104-107
- [9] IUPAC Compendium of Chemical Terminology, 2nd Edition (1997).
- [10] E.G Thorsteinsson, The Nitrogen Discharge. A Global (volume averaged) Model Study, *Electrical and Computer Engineering*, University of Iceland, October 2008.
- [11] N St J Braithwaite, "Introduction to gas discharges", *Plasma Sources Sci. Technol.* 9 (2000) 517-527
- [12] C. H. Kruger, Christophe O. Laux, Lan Yu, Denis M. Packan, Laurent Pierrot "Nonequilibrium discharges in air and nitrogen plasmas at atmospheric pressure," *Pure Applied Chemical.*, 74(3)(2002)337-347.