Numerical simulation of the kinetics of dissociation and ionization of molecular hydrogen in the penning discharge plasma with the use of the reduced kinetic model

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Abstract. A simplified kinetic scheme for describing the kinetics of ionization and dissociation of hydrogen in the Penning discharge plasma is developed. The calculations of the component composition of the Penning discharge plasma are performed. Numerical simulation results are compared with the results provided by the detailed state-to-state kinetic scheme.

1. Introduction
In recent years the increasing interest in the study of the kinetics of molecular hydrogen and its isotopes in low-temperature plasma and Penning discharge has been primarily associated with the development of the electrical devices such as neutron generators and ion sources [1–3]. One of the most important characteristics that define the efficiency of these devices is a chemical composition of the Penning discharge plasma. Component composition of the discharge plasma depends on the characteristic energy of charged particles (electrons and ions) gained by them in the crossed electric and magnetic fields, and determines by the rate of energy exchange with the neutral gas molecules. The complexity of the determination of the component composition in the Penning discharge plasma is due to the need to take into account a large number of kinetic processes describing the collisions of an electron and molecules, molecules and atoms, molecules in various excited states, the complexity of solving the system of kinetic equations, as well as small amount of experimental data on the plasma chemical composition [4–6].

Available papers related to the numerical simulation of atomic-molecular composition of plasma in ion sources mainly concern the devices with high gas-discharge current used in fusion reactors, as well as sources of H− ions [1,5]. At the same time many ion sources used in the gas-filled neutron sources operates at relatively low discharge current (I = 0.1–2 mA) and the use of the detailed kinetic schemes in the compute-intensive 2D and 3D PIC models for calculation of the plasma chemical composition appears to be difficult.

In this paper we consider the Penning discharge at the pressure p ≈ 10−3−10−2 Torr. The potential difference applied between the cathode and the anode is ϕ = 1–3 kV. The current through the
discharge is equal to $I = 0.1 \div 2$ mA, and the ionization degree is $\alpha = 10^2$. In the paper the component composition of the plasma in molecular hydrogen using the state-to-state and the simplified kinetic schemes is calculated. With the use of numerical simulation, the population of vibrational states of the hydrogen molecules, the discharge degree of ionization and dissociation, as well as the impact of various kinetic processes on the plasma component composition were defined.

2. Numerical simulation results
A big number of plasma-chemical processes occur in the area of the Penning discharge [7–11]. First of all it is the processes of direct excitation of vibrationally excited states by electron impact, stepwise mechanism of excitation of vibrationally excited states occurred due to the excitation of the electronic states, the ionization of particles by electron impact, processes of dissociative ionization, dissociation of molecules flowing through the electronically excited states $B'\Sigma_u^+\ldots$, $C'\Pi_u$, $B''\Sigma_u^+$, $D''\Pi_u$, $B''\Sigma_u^+$, $D''\Pi_u$, $b'\Sigma_u^+$, and chemical reactions involving heavy molecules and atoms. In this paper, the kinetic scheme (see table 1) has been developed to describe the kinetics of ionization and dissociation of hydrogen in the Penning discharge plasma.

Calculation of the component composition of the Penning discharge plasma in the zero-dimensional approximation was carried out under the following assumptions:
1) The initial data set included the electron density $N_e^0$ and the concentration of neutral hydrogen molecules. In the calculations the electron density was taken as a constant.
2) The electron energy distribution function (EEDF) was considered either Maxwell distribution function or a combination of Maxwell EDF (simulating thermal electrons produced inside the main discharge volume) and the delta function (describes the fast electrons emitted from the cathode as the result of ion-electron emission). It was assumed that the share of fast electrons is 10%.
3) The energy of thermal electrons was varied within the range of 1÷50 eV, the energy of the fast electrons was considered to be equal to 1 keV, the temperature of neutral molecules and ions was taken to be equal to 300–500 K.
4) The physical time was considered to be equal to 20 microseconds. It corresponds to the pulse width in the ion source based on the Penning discharge.

A detailed analysis of different ionization and dissociation mechanisms in the Penning discharge plasma is given in figure 1. The figure shows that the main mechanisms of atomic ions production are the dissociative ionization processes №2–3. At the same time, with the increase of the electron temperature, the influence of the mechanism №2 on the concentration of atomic ions decreases, and the influence of the mechanism №3 increases. It should be also noted that the share of the process of ionization of neutral atoms by the electron impact in the formation of atomic ions is less than 3%. At low temperatures, the main mechanism of electron molecule dissociation is №10, flowing through the excited electronic state $b'\Sigma_u^+$. With the increase of the electron temperature, hydrogen atoms predominantly produced by the processes of dissociative ionization of molecule №4 and №5, and the mechanism of dissociation №8.

A detailed analysis of the ionization and dissociation mechanisms in the case of non-Maxwell EDF used in the calculations is given in figures 2–3. On the bar charts the influence of various mechanisms of atomic ions production in the hydrogen plasma is shown. It should be noted that the inclusion of the monoenergetic electrons in the kinetic model leads to the increase of the influence of dissociative ionization mechanism №3 on the concentration of atomic ions. Numerical simulations show that in this case the fraction of atomic hydrogen ions produced by the mechanism №3 in the kinetic scheme is equal to 75–85% (see figure 2). Figure 3 shows the influence of different mechanisms on the production of hydrogen atoms. In this case, as in calculations with Maxwell EEDF, it appears that the main mechanisms of dissociation are the mechanisms №6 and №10, as well as the processes of dissociative ionization №2–3.
| Molecule ionization | Dissociation | Processes with participation of heavy particles |
|---------------------|--------------|-----------------------------------------------|
| 1. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub><sup>+</sup> (X<sup>2</sup>Σ<sup>+</sup>) + e | 4. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (B<sup>3</sup>Σ<sup>+</sup>) + e → H(1s) + H(2p) + e | 12. H<sub>2</sub><sup>+</sup> + H → H<sub>2</sub> + H<sup>+</sup> |
| ν<sub>e</sub> = 0 | ν<sub>e</sub> = 0 | K = 9.3×10<sup>6</sup> cm<sup>6</sup>s<sup>-1</sup>[13] |
| 0 ≤ ε ≤ 200 eV | 0 ≤ ε ≤ 200 eV | 13. H+H<sub>2</sub> (ν ≥ 4) → H + H<sub>2</sub><sup>+</sup> |
| Dissociative ionization | 5. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (C<sup>3</sup>Σ<sup>+</sup>) + e → H(1s) + H(2p) + e | K = 2.5×10<sup>6</sup> cm<sup>6</sup>s<sup>-1</sup>[13] |
| 6. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (B<sup>3</sup>Σ<sup>+</sup>) + e → 2H + e | 7. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (D<sup>3</sup>Π<sub>u</sub>) + e → 2H + e | 14. H+H+H<sub>2</sub> → H<sub>2</sub> (X, ν = 14) + H<sub>2</sub> |
| ν<sub>e</sub> = 0 | ν<sub>e</sub> = 0 | K = 2.68×10<sup>31</sup> cm<sup>6</sup>s<sup>-1</sup>[5] |
| 0 ≤ ε ≤ 200 eV | 0 ≤ ε ≤ 200 eV | 15. H+H+H → H<sub>2</sub> (X, ν = 14) + H |
| 8. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (B<sup>3</sup>Σ<sup>+</sup>) + e → 2H + e | 9. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (D<sup>3</sup>Π<sub>u</sub>) + e → 2H + e | K = 8.04×10<sup>31</sup> cm<sup>6</sup>s<sup>-1</sup>[5] |
| ν<sub>e</sub> = 0 | ν<sub>e</sub> = 0 | 16. H<sub>2</sub><sup>+</sup> + H → H<sup>+</sup> + H + H<sub>2</sub> |
| 0 ≤ ε ≤ 200 eV | 0 ≤ ε ≤ 200 eV | CS[13] |
| 11. H + e → H<sup>+</sup> + e + e | 10. H<sub>2</sub> (X<sup>1</sup>Σ<sup>+</sup>, ν<sub>e</sub>) + e → H<sub>2</sub> (b<sup>3</sup>Σ<sup>+</sup>) + e → H(1s) + H(1s) + e | CS[12] |
| CS[12] | ν<sub>e</sub> = 0 | 0 ≤ ε ≤ 1000 eV |

Recombination

17. e+e+H<sup>+</sup> → e + H(n) | K = 6.34×10<sup>-27</sup>n<sup>2</sup> | 18. e+H<sup>+</sup> → H+hv |
| K = 6.34×10<sup>-27</sup>n<sup>2</sup> × | \( \frac{1}{T_{e}^{3} (E_{n}^{2,33} + 4.38E_{n}^{1,72} + 1.32E_{n}^{3})} \) cm<sup>6</sup>s<sup>-1</sup> | K = 3.92×10<sup>-14</sup> \( \frac{1}{n} \times \frac{E_{n}^{1,5}}{E_{n} + 0.35} \) cm<sup>3</sup>s<sup>-1</sup> |
| [12] | | [14] |

19. e+e+H<sub>2</sub><sup>+</sup> → e + 2H | K = 8.75×10<sup>-22</sup>T<sub>e</sub> cm<sup>6</sup>s<sup>-1</sup>[5] |
| 20. e+H<sub>2</sub><sup>+</sup> → H(l) + H(n) | CS[12] |
Figure 1. The fraction of atomic ions produced by the following reactions (EEDF is Maxwell, $T_e = 10$ eV, $N_e = 3*10^{17}$ m$^{-3}$):

1. $H_2 \left( X^1\Sigma_g^+, v \right) + e \rightarrow H_2^+ \left( X^2\Sigma_u^+ \right) + 2e \rightarrow H(1s) + H^+ + 2e$
2. $H_2 \left( X^1\Sigma_g^+, v \right) + e \rightarrow H_2^+ \left( ^2\Sigma_u^+ \right) + 2e \rightarrow H(1s) + H^+ + 2e$
3. $H + e \rightarrow H^+ + e + e$
4. $H_2^+ + H \rightarrow H_2 + H^+$

Figure 2. The fraction of atomic ions produced by the following reactions (EEDF is Nonmaxwell, $T_e = 10$ eV, $N_e = 3*10^{16}$ m$^{-3}$):

1. $H_2 \left( X^1\Sigma_g^+, v \right) + e \rightarrow H_2^+ \left( X^2\Sigma_u^+ \right) + 2e \rightarrow H(1s) + H^+ + 2e$
2. $H_2 \left( X^1\Sigma_g^+, v \right) + e \rightarrow H_2^+ \left( ^2\Sigma_u^+ \right) + 2e \rightarrow H(1s) + H^+ + 2e$
3. $H + e \rightarrow H^+ + e + e$
4. $H_2^+ + H \rightarrow H_2 + H^+$

It is worth noting that the vibrational distribution function of hydrogen molecules, in contrast to the glow discharge, has no significant effect on the kinetics of plasma chemical processes in the Penning discharge. Most chemical processes (ionization, dissociation, excitation of the electronic states) take place with the participation of hydrogen molecules in the ground vibrational state. However, with the increase of the electron temperature and concentration, the number of vibrationally excited molecules increases and, consequently, its influence on the kinetics of plasma-chemical reactions also increases.

Nevertheless, calculations carried out in this paper show that the relative share of neutral atoms and ions produced in reactions with participation of vibrationally excited molecules is less than 10%. It should be also noted that some dissociation mechanisms provided in the kinetic scheme, produce more than 40% of neutral atoms from vibrationally excited states, however, these reactions do not
significantly affect the concentration of hydrogen atoms. Figure 4 gives the vibrational distribution function in the Penning discharge plasma.

Figure 3: The fraction of neutral atoms produced by the following reactions (EEDF is nonmaxwell, $T_e = 3$ eV, $N_0 = 3 \times 10^6$ m$^{-3}$)

1. $H_2(X^3\Sigma_g^+,v_i) + e \rightarrow H_2^+(X^2\Sigma_g^+) + 2e \rightarrow H(1s) + H^+ + 2e$
2. $H_2(X^1\Sigma_g^+,v_i) + e \rightarrow H_2^+(3\Sigma_u^+) + 2e \rightarrow H(1s) + H^+ + 2e$
3. $H_2(X^3\Sigma_g^+,v_i) + e \rightarrow H_2(B^1\Sigma_u^+) + e \rightarrow H(1s) + H(2l) + e$
4. $H_2(X^1\Sigma_g^+,v_i) + e \rightarrow H_2(C^1\Pi_u) + e \rightarrow H(1s) + H(2l) + e$
5. $H_2(X^3\Sigma_g^+,v_i) + e \rightarrow H_2(B^3\Sigma_u^+) + e \rightarrow 2H + e$
6. $H_2(X^1\Sigma_g^+,v_i) + e \rightarrow H_2(D^3\Pi_u) + e \rightarrow 2H + e$
7. $H_2(X^3\Sigma_g^+,v_i) + e \rightarrow H_2(B^3\Sigma_u^+) + e \rightarrow 2H + e$
8. $H_2(X^1\Sigma_g^+,v_i) + e \rightarrow H_2(D^3\Pi_u) + e \rightarrow 2H + e$
9. $H_2(X^3\Sigma_g^+,v_i) + e \rightarrow H_2(B^3\Sigma_u^+) + e \rightarrow H(1s) + H(1s) + e$
10. $e + H_2^+ \rightarrow H + H(n)$
11. $e + e + H^+ \rightarrow e + H(n)$
12. $e + H^+ \rightarrow H + h\nu$

Figure 4: Vibrational distribution function (EEDF is Maxwell) for different electron temperature: $T_e = 50$ eV (squares), $T_e = 10$ eV (circles).
In the case the molecular ions of hydrogen can achieve sufficiently high energies (more than 100 eV) the process $H_2^+ + H_2 \rightarrow H^+ + H + H_2$ can have a significant impact on the plasma chemical composition.

3. Conclusion
On the basis of the work done in this article, a simplified kinetic model was developed. The model allows to calculate the chemical composition of Penning discharge plasma in molecular hydrogen. The developed simplified kinetic model includes five components and 20 reactions. The work is performed under the grant of the Russian Science Foundation, the project № 16–11–10275.

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