

NON-EQUILIBRIUM PLASMA-CHEMICAL REACTIONS IN HIGH PRESSURE
SYSTEMS PROVIDED BY VIBRATIONALLY EXCITED REAGENTS

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The essential role of vibrational excitation in kinetics and energetics of chemical reactions in a slowly ionized non-equilibrium high pressure plasma is shown in the present work. The reactions rate constants of vibrationally excited reagents are calculated in the framework of the statistical theory. The specific application of suggested model is considered for the chemical reactions of synthesis and of direct reduction of elements. We obtain the parameter values, when the power effectiveness and yield are optimal.

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The requirements of productivity and simplification of technology explain the interest to non-equilibrium high pressure plasma chemical systems (≥ 1 atm.). The electron energy is not sufficient as a rule for electronic excitation and dissociation in such discharge systems. For this reason the total energy input (for the non-electronegative gases - N_2, CO, CO_2, H_2 etc.) can be concentrated in the vibrational degrees of freedom. Plasma chemical reactions caused by vibrationally excited reagents have the following advantages over other types of reactions:

1) Energy threshold of such processes is usually lower than that of electronic excitation. For example, vibrationally excited H_2 requires for dissociation 4,4 eV, while hydrogen dissociation through electronic excited state $b^3 \Sigma_g^+$ needs 8,8 eV.

2) The top cross section of vibrational excitation lies in the range of 1-3 eV and the main discharge energy is therefore concentrated in the vibrational degrees of freedom. Electronic excitation consumes usually more than 10 eV of electron energy and besides this results simultaneously in the extra energy input in subordinate channels - ionization, excitation, dissociation etc.

3) Vibrational energy of reacting molecules is the most essential in overcoming endothermic reactions activation threshold [1].

Considered mechanism can be the main one both in plasma-

chemical synthesis and in direct reduction of elements from their compounds. For example let us consider the nitrogen oxides synthesis in mixture N_2-O_2 . Such a synthesis can be realized by the number of elementary reactions, where the N-N breaking off is the limiting stage. For vibrationally excited nitrogen such a stage is:



The alternative reactions are those provided by electronically excited and charged species:



The dependence of reaction (1) cross section on the level ν of vibrational excitation can be obtained within the framework of the statistical theory of bimolecular reactions [2]:

$$\sigma_R(\nu, \epsilon_T) = \sigma_0 \rho(\nu) \frac{(\hbar\omega\nu + \epsilon_T - E_a)^2 \Theta(\hbar\omega\nu + \epsilon_T - E_a)}{(\hbar\omega\nu + \epsilon_T)^2} \quad (3)$$

where ϵ_T is the thermal energy, $E_a = 3eV$ is the activation threshold of reaction (1), ω - is the vibration frequency of N_2 , σ_0 is the geometry cross section of molecular ground state, $\rho(\nu)$ - is the geometry cross section increase with level rise, $\Theta(\epsilon)$ - is the steep function.

Reaction (1) rate constant can be calculated for Maxwell distribution of molecular velocities and presented in such a form:

$$\frac{k_R}{k_0(T_0)} = \int_0^{E_a/\hbar\omega} \rho(\nu) f_\nu(\nu) \frac{T_0^2}{E_a^2} \exp\left[-\frac{\hbar\omega\nu - E_a}{T_0}\right] d\nu + \int_{E_a/\hbar\omega}^{\infty} \rho(\nu) f_\nu(\nu) \left[\frac{\hbar\omega\nu - E_a}{E_a}\right]^2 d\nu \quad (4)$$

where $k_0(T_0)$ is the elastic scattering rate constant dependence on translational temperature T_0 . If the vibrational excitation distribution is the Treanor one:

$$f_v(v) = A \exp\left(-\frac{\hbar\omega v}{T_v} + \frac{\hbar\omega x_e}{T_0} \left(v + \frac{1}{2}\right)^2\right) \quad (5)$$

and molecular unharmonism is rather small $x_e \ll T_0 \hbar\omega / T_v E_a$ then for vibrational temperature T_v we get:

$$\frac{k_R(T_v)}{k_0(T_0)} = \rho\left(\nu = \frac{E_a}{\hbar\omega}\right) \frac{T_v}{E_a} \left[1 + \left(\frac{T_0}{T_v}\right)^3\right] \quad (6)$$

Relationship (6) for $T_0 = T$ gives the known dependence

$k_R(T_0)$ coinciding with the experimental data [3]. The energy balance in the system is:

$$n_0 \frac{dT_v}{dt} = n_e n_0 k_{ev} \hbar\omega - n_0 [O] k_0(T_0) \rho T_v e^{-\frac{E_a}{T_v}} - k_{vT} n_0^2 \hbar\omega \quad (7)$$

where n_e , n_0 , $[O]$ are the electrons, nitrogen molecules, and oxygen atoms concentrations; k_{vT} , k_{ev} - vibrational relaxation and excitation constants.

The V-T relaxation energy losses can be neglected in comparison with reaction input, when:

$$T_v > T_{vmin} = E_a \ln^{-1} \left\{ \frac{k_0(T_0)}{k_{vT}} \cdot \frac{[O]}{n_0} \cdot \rho \cdot \frac{T_{vmin}}{\hbar\omega} \right\} \quad (8)$$

In this case the rate of reaction (1) can be calculated by

$$V_R = n_e n_0 k_{ev} \frac{\hbar\omega}{E_a} \quad (9)$$

It's easy to verify that the reaction rate (9) is much greater than that of (2).

The total set of the reaction forming nitrogen oxides synthesis are:



It's clear that synthesis (10) may be realized by explosion mechanism. But the increase of $[O]$ concentration does not lead to self-acceleration of the total reaction because of energy input in N_2 restrictions.

The energetic efficiency of considered processes and their yields are controlled by energy input in discharge for fixed

pressure. But energy input is confined by both vibrational relaxation (8) and requirements of products stability with respect to reverse reactions. The yield (X) and efficiency (η) dependence on energy input are represented in fig.1,2, ($n_0 = 3 \cdot 10^{19} \text{ cm}^{-3}$) for non-equilibrium volume discharges. These results are in agreement with the experimental data obtained in powerful non-equilibrium discharges, for example, sustained by relativistic electron beam (pressure 1 - 6 atm) [4] or in UHF-discharge with magnetic field (pressure $\sim 0,1$ atm.) [5].

Nitrogen dissociation can be simplified by the preliminary weakening of N-N bond, when composite compounds are formed. Thus, ammonia synthesis may be realized in $\text{N}_2\text{-H}_2$ mixture with intermediate N_2H_2 and N_2H_4 formation when there is weakening of bond from 10eV to 2.5eV. Such a synthesis was observed in high pressure non-equilibrium plasma [4].

Let us consider the elements reduction from their oxides. It is the other important class of chemical reactions realized in non-equilibrium high pressure plasma by vibrationally excited reagents. Reduction of carbon from CO and CO_2 can be regarded as an example of such reactions. The complexity of carbon reduction from CO can be explained by high bond energy ($\sim 10\text{eV}$) for this molecule. On the other hand CO has a very high rate of vibrational excitation by electron impact ($k_{ev} = 10^{-7} \text{ cm}^3/\text{sec.}$). Therefore the following channel exists:



Such a reaction was experimentally realized in non-equilibrium plasma [6]. The dependence of the reaction (11) cross section on the levels V_1, V_2 of reagents vibrational excitation can be

defined within the framework of the bimolecular reactions statistical theory [1] :

$$G(\nu_1, \nu_2) = \left[\frac{\hbar\omega_{CO}(\nu_1 + \nu_2) - E_a}{\hbar\omega_{CO}(\nu_1 + \nu_2)} \right]^2 \frac{\omega_{CO}^2}{\omega_{CO_2}^2} \theta[\hbar\omega_{CO}(\nu_1 + \nu_2) - E_a] \quad (12)$$

where ω_{CO} and ω_{CO_2} are the main frequency of vibration of CO and CO_2 , $E_a \approx 6\text{eV}$ - is the reaction (11) activation

threshold. Taking into account Treanor distribution (5) for reaction (11) we get:

$$k_R = k_0(T_0) \left(\frac{T_v}{E_a} \right)^2 \frac{\omega_{CO}^2}{\omega_{CO_2}^2} \exp \left[- \frac{\hbar\omega_{CO} T_0}{4\chi_e} \cdot \frac{1}{T_v^2} \right] \quad (13)$$

Energy balance equation (similar to (7)) gives the restriction on T_v (similar to (8)).

$$T_v^2 > T_{vmin}^2 = \frac{\hbar\omega_{CO} T_0}{4\chi_e} \ln^{-1} \left[\frac{k_0(T_0) (\omega_{CO})^2 T_{vmin}^2}{k_{vr} (\omega_{CO_2} \hbar\omega_{CO} E_a)} \right] \quad (14)$$

For $T_0 = 10^2\text{K}$, $n_0 = 3 \cdot 10^{19}\text{cm}^{-3}$ we have $T_v \text{ min} \approx 0,2\text{ eV}$ and the least energy input $W_{\text{min}} \approx 1\text{ j/cm}^3$. The yield and efficiency of considered process can be calculated by:

$$\chi = 2 \frac{T_v - T_{vmin}(1-\chi)}{E_a}; \quad \eta \approx \left(1 - \frac{T_{vmin}}{T_v} \right) \theta(T_v - T_{vmin}) \quad (15)$$

For $n_0 = 3 \cdot 10^{19}\text{cm}^{-3}$, and energy input $W \approx 2\text{ j/cm}^3$
 $\chi = 10\%$, $\eta \approx 50\%$.

Carbon reduction from CO_2 requires (16) in addition to (11):



It is realized by the following elementary processes:



The reaction (17) has $E_a = 5,5\text{ eV}$ and is the limiting stage here. At the same time to realize this reaction through the

electronic excited states $^1A_1 (\Delta_g)$ and $^1B_1 (\Sigma_g^-)$ - the energy threshold become $\sim 9\text{eV}$. If $T_{v\text{min}} < T_v < \Delta Q$ then process (16) efficiency is:

$$\eta = 1 + \frac{T_{v\text{min}}}{\Delta Q} - \frac{T_v}{2E_a} - \frac{T_{v\text{min}}}{T_v} \quad (19)$$

The best $\eta_{\text{max}} = 80\%$ is reached when $T_v = \left[2E_a T_{v\text{min}} \right]^{\frac{1}{2}}$ (2eV). Carbon reduction from CO and CO₂ was experimentally considered in [5], where $\eta \approx 60\div 70\%$. The carbon yield dependence on CO₂ concentration (energy input is fixed) is represented in fig.3 [5].

Thus, it is shown that vibrational excitation of reagents is very essential in non-equilibrium high pressure plasma chemistry. It is related both to reactions of synthesis and elements reduction from their compounds. This results allow to claim that considered reactions are of practical interest. The optimal values of parameters are obtained. Particularly, if energy input is $1 - 3 \frac{j}{\text{cm}^3 \text{atm}}$ then for synthesis - $X \approx 10\%$, $\eta \approx 30\%$ and for reduction considered $\eta \approx 50 \div 80\%$.

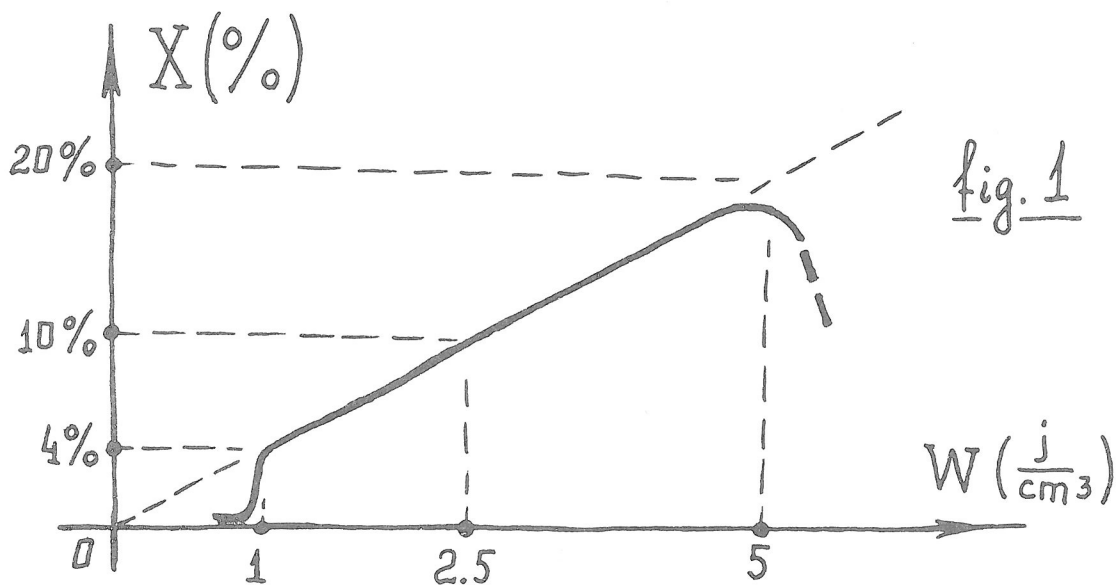


fig. 1

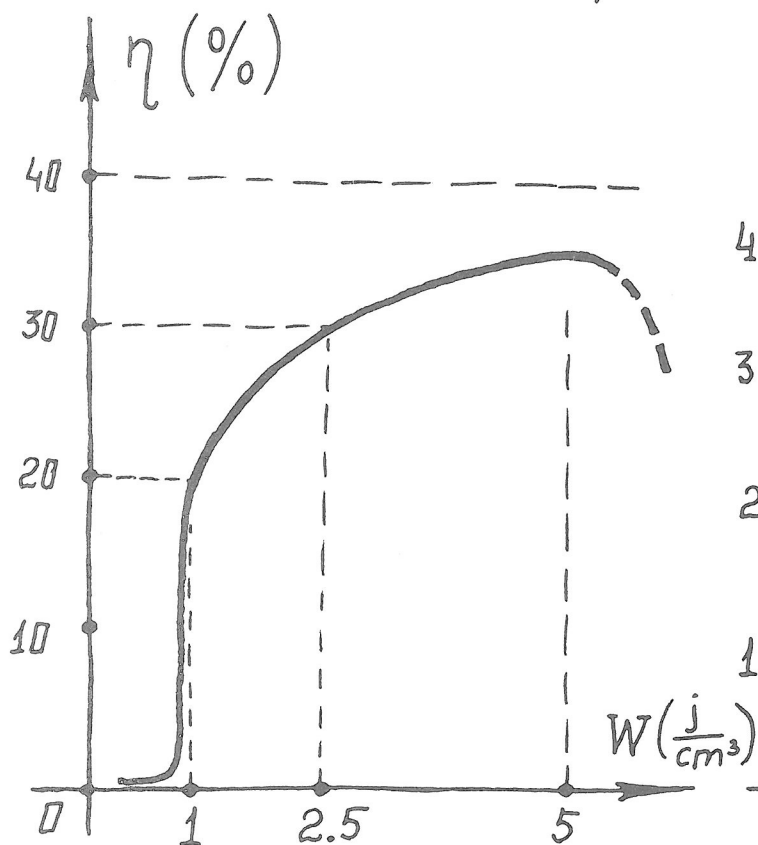


fig. 2.

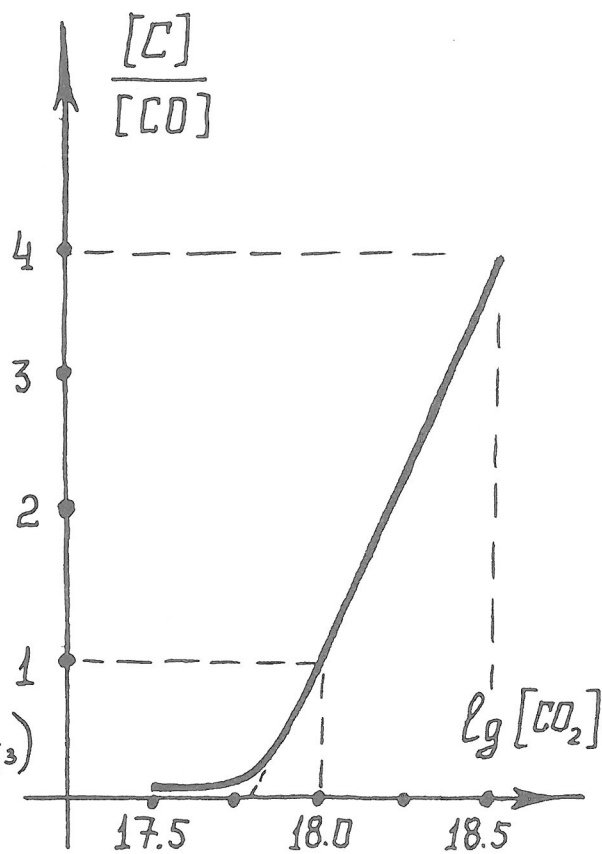


fig. 3.

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