Mathematical Modeling of Plasmachemical Processes

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Abstract

In this research, we studied the kinetics of plasmachemical processes in quasiequilibrium and nonequilibrium conditions. The example of methane conversion into acetylene showed that the most efficient plasmachemical process may be achieved under nonequilibrium conditions, especially, when the reaction was stimulated by vibrational excitation of molecules.

Key Words: Methane, acetylene, radio frequency discharge, energy efficiency, vibration-translational nonequilibrium.

1. Introduction

The use of low temperature plasma medium for the stimulation of chemical reactions gives the possibility to develop processes of synthesis and dissociation of some inorganic compounds, processes of thin layer organic synthesis, polymerization and, even,fuel production as well. High energy density and specific output are the main characteristic features and advantages of plasmachemical systems. The capacity of modern plasmatrons reach more than 10^4 kW for electroarc and 10^3 kW for high frequency discharges in stationary conditions of small sizes [1]. At the same time, the specific output from gas phase plasmachemical processes has reached 10 m^3/h of gas-product on 1 cm^3 of active volume of plasma.

To achieve of highly effective chemical processes in plasma one must have a detailed comprehension of the mechanism kinetics through the diversity of physicochemical transformations in the systems considered.

One possible way to investigate such a system is via the mathematical modeling of the plasmachemical processes. Mathematical modeling of complex plasmachemical processes allows one to create models and thus to diminish the number of what otherwise could be expensive experiments.

The present work is dedicated to the elaboration, selection and application of mathematical modeling methods for the investigation of plasmachemical reaction kinetics in quasiequilibrium and nonequilibrium conditions.

2. Formulation of the Problem

Traditional plasma-chemical investigations have been carried out in quasiequilibrium plasma of electrical arcs and high frequency discharges at high pressure, where plasma played the role of initial preheating agent. But today it's quite evident that nonequilibrium plasmachemical systems are of great interest to both theoretical and applied viewpoints, as it permits one to selectively apply chemical conversions with high energy efficiency. High vibrational temperature of these systems lead to high speed direct processes of useful products. Low translational temperature prevents irreversible reactions, and provides the stability of products, formed in nonequilibrium plasma.

2.1. Mathematical Modeling of Quasiequilibrium Plasma-chemical Processes

Mathematical modeling of chemical processes in the streams of low temperature plasma leads to a solution of the system for hydrodynamic and chemical kinetic equations describing these processes. It is well known that there is no general method to solve the set of hydrodynamic equations. That is why they are usually limited to approximate solutions, for which partial differential equations may be transformed to ordinary differential equations. One-dimensional flow of gas is one such case. With the gas flow considered laminar, external forces and radiation are not a concern. It is assumed that, at point $x = 0$, there is a definite composition of gas mixture, with homogeneous jet section and initial concentrations of substances, initial rate, temperature and pressure. That is, we suppose the mixture is momentarily heated up to the temperature sufficient for reaction.

The system of one-dimensional stationary equations for plasma flow, in which the chemical reactions proceed can be written as follows [2]:

$$\text{equation of flow continuity:} \quad \frac{d}{dx}\left(\rho v\right) = 0 \tag{1}$$

$$\text{equation of } i \text{ }^{\text{th}} \text{ component continuity:} \quad \frac{d}{dx}\left[n_i\left(v + V_i\right)\right] = K_i \tag{2}$$

$$\text{equation of motion:} \quad \rho v \frac{dv}{dx} + \frac{dP_{xx}}{dx} = 0 \tag{3}$$

$$\text{equation of energy:} \quad \rho v \frac{dU}{dx} + \frac{d}{dx}\left(P_{xx}v\right) + \rho v^2 \frac{dv}{dx} + \frac{dq}{dx} = 0 \tag{4}$$

$$\text{equation of state:} \quad p = nkT. \tag{5}$$

Here, ρ is mass density of the gas; v is rate of flow; V_i is the rate of diffusion; n_i is the number of i th type molecules in the gas volume unit; P_{xx} is xx-component of the pressures tensor; q is the heat stream; U is the thermodynamical internal energy of the mass unit of substanse; p is the hydrostatical pressure of the gas; T is the temperature of the gas; k is the Boltzmann constant; and K_i is the formation rate of i th type molecules in the unit volume of the mixture in unit time due to chemical reactions, defined by the equations

$$K_i = \sum_j \left(\eta_{ij} - \beta_{ij}\right)\omega_j, \tag{6}$$

where η_{ij} and β_{ij} are stockhiometrical coefficients. The rate of the j 'th reaction ω_j is equal to

$$\omega_j = k_j \left(n_1\right)^{\beta_{1j}} \left(n_2\right)^{\beta_{2j}} - k_j' \left(n_1\right)^{\eta_{1j}} \left(n_2\right)^{\eta_{2j}}, \tag{7}$$

where k_j and k_j' are rate constants of the forward and backward reactions, respectively.

For chemical reaction rate constants we use the Arrhenius equation. Disturbance of the initial equilibrium distribution in the system does not play a practical role at temperatures below 1000 K, but is of high importance at higher temperatures. So for every case, use of the Arrhenius equation and other correlations, based upon the notion of equilibrium static mechanics and thermodynamics, need to be proved.

Equations (1)-(5), with initial conditions given, is a Cauchy problem of ordinary nonlinear differential equations of second order. Their nonlinear character is essential: for, the chemical reaction rate constants have exponential dependence on temperature. The appraisal of the dissipative terms (the diffussion, the heat conduction and the viscosity) in transport Equations (1)-(5) shows that these terms are insignificant under certain (see Eq. (29)) conditions and they may be neglected in comparison with the inertial terms. Then Equations (1)-(5) may be written as a system of first order and solved by one of the methods of numerical integration. It is just this solution, the so-called first approximation, that is considered in the present work.

2.2.   Mathematical Modeling of Nonequilibrium Plasmachemical Processing

The practical realization of endoergic plasmachemical processes emphasizes the primary importance of energy minimization in order to obtain a useful product; and process optimization, to achieve the highest energy efficiency. Energy efficiency optimization of the process can't be realized in the limits of traditional quasiequilibrium plasmachemistry, since, in this case, the product output is limited by thermodynamical equilibrium composition of heated gases. The input energy is distributed to all degrees of molecular freedom, and high rates of nonadiabatic cooling cause the quasiequilibrium systems not to attain high efficiency endoergic reactions. Thus it is necessary to control this process over a wide range to minimize the loss of the energy. It is possible to achieve this in nonequilibrium discharges where the chemical conversions are selected via, say, mainly one distinguished mechanism. This special chemical process mechanism taking place in nonequilibrium plasma is stimulated by oscillatory excitation of basic states of molecules. This mechanism permits the realization of chemical conversions in plasma with extreme energetic efficiency [3]. There are several degrees of descriptions of kinetics of such plasmachemial systems. The most real and consistent one is the use of nonequilibrium chemical kinetics, where molecules are in different quantum states as if they were different kinds of particles.

As far as the kinetic description of complicated chemical systems, this approach has difficulties due to the absense of information concerning the coefficients of process rates, and considerable mathematical problems connected with the solution of ordinary differential equations of large dimensions. The most expedient is the introduction of several temperatures of vibrationally excited molecules (translational, and one or several vibrational) into the mathematical model. The system of equations then include the equations of chemical kinetics, gas dynamics and energy balance for translational and vibrational energies:

$$\frac{d}{dx}\left(\rho v\right) = 0 \quad \text{equation of flow continuity} \tag{8}$$

$$\rho v \frac{d}{dx}\left(\frac{\rho_i}{\rho}\right) = \frac{M_i}{N_A}K_i \quad \text{equation of i}^{\,th} \text{ continuity component} \tag{9}$$

$$\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0 \quad \text{equation of motion} \tag{10}$$

$$\rho v \frac{d}{dx}\left(\varepsilon_t + \frac{p}{\rho} + \frac{v^2}{2}\right) = \alpha\varepsilon_R + \varepsilon_{VT} \quad \text{equation of translational energy} \tag{11}$$

$$\rho v \frac{d}{dx}\varepsilon_v = \varepsilon_{eV} - \varepsilon_R - \varepsilon_{VT} \quad \text{equation of vibrational energy} \tag{12}$$

$$p = \frac{\rho}{M}RT_0 \quad \text{equation of state,} \tag{13}$$

where ε_R, ε_{VT}, ε_{eV} are chemical reaction, VT-relaxation and vibrational excitation energies, respectively. Here, the first two are supposed to be

$$\varepsilon_R = k_R n^2 \Delta Q \tag{14}$$

$$\varepsilon_{VT} = k_{VT} n^2 \hbar\omega_I. \tag{15}$$

Let's further assume

$$\varepsilon_{eV} = k_{eV} n_e n \hbar\omega_{II}, \tag{16}$$

which corresponds to vibrational energy pumping by electronic shock [4]. The coefficients of reaction rate, VT-relaxation and vibrational excitation are denoted by k_R, k_{VT} and k_{eV}, respectively; and n_e denotes the concentration of electrons, which is a parameter in this problem; ΔQ is the value of vibrational energy for one act of reaction; T_v and T_0 are vibrational and translational temperatures; ε_v and ε_t are vibrational and translational energies of gas; ω_I is frequency of deformative vibrations responsible for VT-relaxation; and ω_{II} is frequency of molecular vibrations excited by electronic shock. For a description of the influence of vibrational excitation of the reagents on the chemical reaction rate coefficient, we introduce empirical dimensionless parameter α, the coefficient of vibrational energy efficiency, which varies from 0 to 1, and characterizes the vibrational energy fraction that effectively takes part in the overcoming of the activational barrier of the reaction. The equation of translational energy takes into account gas heating in the process of VT-relaxation and heat effects of chemical reactions. The equation of vibrational energy takes into account the electron-shocked excitation, the energy loss for chemical conversions and VT-relaxation.

Equations (8)-(13), with their initial conditions, is a Cauchy problem of ordinary nonlinear differential equations. In the considered range of temperatures and flow rates, this system of differential equations contains equations in which the absolute values of the right hand sides may vary several tens of orders. This, of course, raises the question of the reliability of the calculated results. Most of the existing numerical methods of the Cauchy problem are not used in situations such as this because their errors affect the results. Instead, we use a "hard" method [5] based on the so-called "predictor-corrector" idea suggested by Geer [6]. This method was mainly used in our investigation. Results were controled by comparing values obtained via different methods. These methods were Adam's method of the sixth order, Runge-Kutta's method of the fourth order, and modified method of Runge-Kutta-Fehlberg [7]. All of them showed qualitatively the same behavior of kinetic and thermodynamics curves, and quantitatively highly satisfactory coincidence.

3. Mathematical Modeling of Methane Conversion into Acetylene

The process of methane conversion into acetylene has been studied in quasiequilibrium and nonequilibrium systems, stimulated by the vibrational excitation of molecules. Calculations were made in accordance with the general statements developed in the previous sections.

Methane conversion into acetylene has been actively investigated for thirty years. Interest in the process is driven by the practical necessity to develop new technologies for the synthesis of chemical raw materials and artificial fuels from natural gas. The primary focus of many theoretical and practical investigations of methane conversion into acetylene has been the reduction of energy costs and increase in conversion efficiency. So, optimization of methane conversion in the quasiequilibrium plasma of electrical arcs at atmospheric pressure under the aforementioned conditions suggests it will be possible to obtain a 76% conversion using only 8 eV/mol C_2H_2 [8, 9]. Investigation into radio frequency discharge-generated nonequilibrium plasma at moderate pressure establishes the possibility to efficiently convert methane into acetylene at only 6 eV/mol C_2H_2 [10]. It was shown, that the 40% decrease in energy expence for C_2H_2 production with respect to the one in quasiequilibrium plasmachemical system is due to vibrational-translational nonequilibrium.

3.1. Methane into Acetylene Conversion in Quasiequilibrium Plasma

Kinetic calculations for the conversion of methane into acetylene in an arc discharge were, as suggested by Cassel [11], performed with the following formal scheme:

$$2CH_4 \quad \rightarrow \quad C_2H_6 + H_2 \tag{17}$$
$$C_2H_6 \quad \rightarrow \quad C_2H_4 + H_2 \tag{18}$$
$$C_2H_4 \quad \rightarrow \quad C_2H_2 + H_2 \tag{19}$$
$$C_2H_2 \quad \rightarrow \quad 2C + H_2 \tag{20}$$

This scheme describes the "brutto"-reaction sequence of methane pyrolysis, where acetylene is considered to be an intermediate product. Thus, in order to get acetylene from methane in a plasma, the process should be interrupted after the Equation (19). Consequently, the maximum acetylene concentration in the plasma must have been reached by this point.

Then conservation Equations (1)-(5), with mechanism (17)-(20) of methane decomposition in mind, after simple transformations, can be rewritten as follows for the weight fractions C_i, temperature T and duration of the process t:

$$\frac{dC_1}{dx} = -\frac{1}{v}k_1C_1 \tag{21}$$

$$\frac{dC_2}{dx} = \frac{1}{v}\left(\frac{1}{2}\frac{M_2}{M_1}k_1C_1 - k_2C_2\right) \tag{22}$$

$$\frac{dC_3}{dx} = \frac{1}{v}\left(\frac{M_3}{M_2}k_2C_2 - k_3C_3\right) \tag{23}$$

$$\frac{dC_4}{dx} = \frac{2}{v}\frac{M_4}{M_3}k_3C_3 \tag{24}$$

$$\frac{dC_5}{dx} = \frac{1}{v}\left(\frac{M_5}{M_1}k_1C_1 + \frac{M_5}{M_2}k_2C_2 + \frac{M_5}{M_3}k_3C_3\right) \tag{25}$$

$$\frac{dT}{dx} = -\frac{\left(\frac{B}{A} - 2v\right)\sum_{i=1}^{5}\sum_{j=-1}^{8}\frac{dC_i}{dx}\left(h_{ij}T^j + h_i^o\right) + vRT\sum_{i=1}^{5}\frac{1}{M_i}\frac{dC_i}{dx}}{\left(\frac{B}{A} - 2v\right)\sum_{i=1}^{5}\sum_{j=-1}^{8}C_ih_{ij}T^{j-1}j + vR\sum_{i=1}^{5}\frac{C_i}{M_i}} \tag{26}$$

$$\frac{dt}{dx} = \frac{1}{v}. \tag{27}$$

Here, $C_1 - C_5$ are weight fractions of substances CH_4, C_2H_4, C_2H_2, C and H_2, respectively, in the gas mixture, where $C_i = m_in_iV/\rho V = m_in_i/\rho = \rho_i/\rho$; $M_1 - M_5$ are molecular weights of these substances; $k_1 - k_3$ are reaction rate constants for reactions (17)-(20); A and B are constants of integration; R is the universal gas constant; and $H_i = \sum_{i=-1}^{8}h_{ij}T^j + h_i^0$ is the enthalpy of 1 g of the ith component.

The rate of flow is determined by the equation (see the Appendix)

$$v = \frac{B}{2A} - \sqrt{\left(\frac{B}{2A}\right)^2 - RT\sum_{i=1}^{5}\frac{C_i}{M_i}}. \tag{28}$$

Equations (21)-(27) were numerically integrated with the initial conditions

$$\begin{aligned}
C_1(0) &= 0.95, \quad C_2(0) = C_3(0) = C_4(0) = 0 \\
C_5(0) &= 0.05, \quad T(0) = 3\cdot10^3 \text{ K} \\
v(0) &= 3\cdot10^4 \text{ cm/s}, \quad t(0) = 0
\end{aligned} \tag{29}$$

using the Runge-Kutta and Adams-Shtermer methods, automatically choosing the steps with 10^{-3} - 10^{-4} relative precision that provides 1-2% solution precision [12]. The solution of the problem was made under the following values for the reaction rate constants:

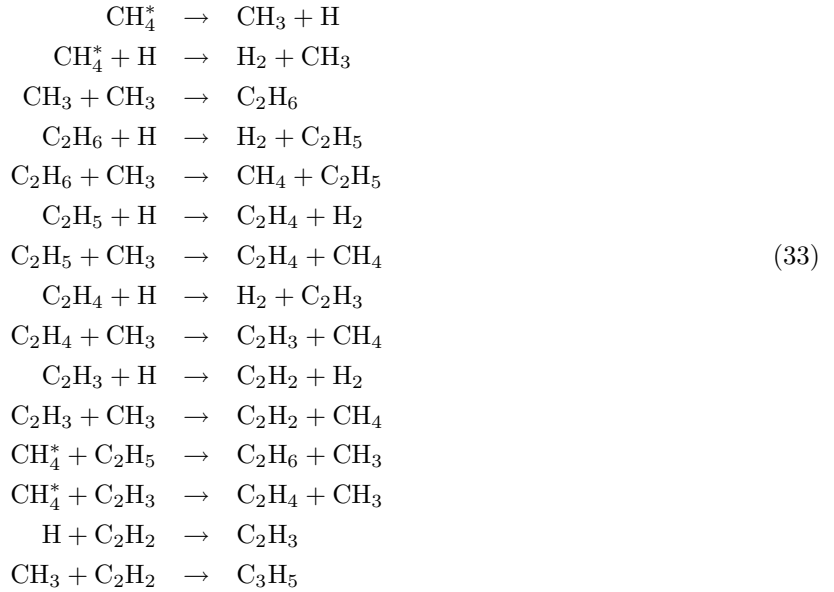$$k_1 = 4.5\cdot10^{13} \exp\left(-\frac{91\cdot10^3}{RT}\right) \tag{30}$$

$$k_2 = 2.57\cdot10^8 \exp\left(-\frac{40\cdot10^3}{RT}\right) \tag{31}$$

$$k_3 = 1.7\cdot10^6 \exp\left(-\frac{30\cdot10^3}{RT}\right). \tag{32}$$

The coordinate where the integration process stops was chosen according to the character of the given problem. In our case, the acetylene concentration curve (see Figure 1) shows that the integration should stop at the point where the acetylene maximum concentration begins decreasing after the maximum point. In practice this means the forced hardening of acetylene is required.

## 3.2.   Methane into Acetylene Conversion in Nonequilibrium Plasma

Conversion in an arc plasma generator is an isenthalpic process: the gas is first heated to 3000 K, which is enough to sustain the process, and provides a condition where the chemical reaction can go on at constant enthalpy of gas mixture. Endoergic chemical reactions of methane decomposition by Cassel's scheme absorb energy and the temperature of the mixture decreases.   Thus, chemical autohardening takes place in the system. As a result, as the temperature decreases to 2000 K the reactions decelerate, though the enthalpy is enough till the end of the reaction, and some part of methane remains unreacted. For their decomposition the initial temperature should be raised and gas must be overheated. In radio frequency discharge (unlike the arc discharge) energy extraction and reaction zones coincide. This fact makes it possible to maintain a constant optimal temperature for the process and, at the same time, the radio frequency discharge pressure permits breaking of the vibratioanal and translational gas temperatures [13]. This will cause stimulation of the endoergic reaction of methane dissociation at low translational temperature. In order to determine the parameters of the temperature break effect, and the parameters to decrease energy expense, we developed a mathematical modeling of methane conversion under vibrational-translational nonequilibrium conditions. After a study of more than 300 reactions, involving vibratiolally excited molecules, we propose that the mecanism of methane conversion will follow the following paths [14]:

$$
\begin{aligned}
CH_4^* &\rightarrow CH_3 + H \\
CH_4^* + H &\rightarrow H_2 + CH_3 \\
CH_3 + CH_3 &\rightarrow C_2H_6 \\
C_2H_6 + H &\rightarrow H_2 + C_2H_5 \\
C_2H_6 + CH_3 &\rightarrow CH_4 + C_2H_5 \\
C_2H_5 + H &\rightarrow C_2H_4 + H_2 \\
C_2H_5 + CH_3 &\rightarrow C_2H_4 + CH_4 \\
C_2H_4 + H &\rightarrow H_2 + C_2H_3 \\
C_2H_4 + CH_3 &\rightarrow C_2H_3 + CH_4 \\
C_2H_3 + H &\rightarrow C_2H_2 + H_2 \\
C_2H_3 + CH_3 &\rightarrow C_2H_2 + CH_4 \\
CH_4^* + C_2H_5 &\rightarrow C_2H_6 + CH_3 \\
CH_4^* + C_2H_3 &\rightarrow C_2H_4 + CH_3 \\
H + C_2H_2 &\rightarrow C_2H_3 \\
CH_3 + C_2H_2 &\rightarrow C_3H_5
\end{aligned}
\tag{33}
$$

With mechanism (33) in mind, after simple transformations, conservation Equations (8-13) can be rewritten as follows (see the Appendix for details):

$$
\begin{aligned}
\frac{dC_1}{dx} = {}& -\frac{1}{v}k_1^\star C_1 - \frac{AN_A}{v^2}\left(\frac{1}{M_3}k_2^\star C_1 C_3 - \frac{M_1}{M_2 M_5}k_5 C_2 C_5 - \right. \\
& - \frac{M_1}{M_2 M_6}k_7 C_2 C_6 - \frac{M_1}{M_2 M_7}k_9 C_2 C_7 - \frac{M_1}{M_2 M_8}k_{11}C_2 C_8 + \\
& \left. + \frac{1}{M_6}k_{12}^\star C_1 C_6 + \frac{1}{M_8}k_{13}^\star C_1 C_8 \right)
\end{aligned}
\tag{34}
$$
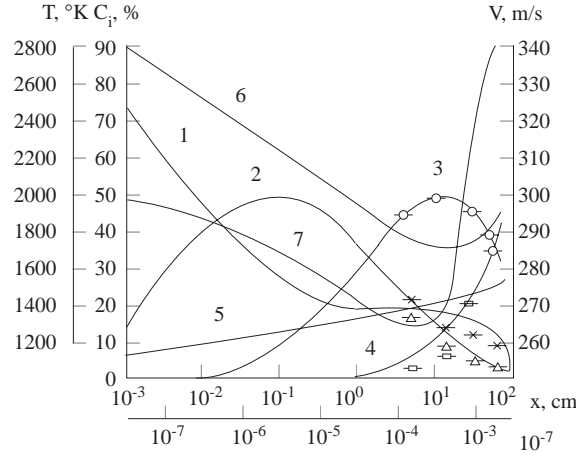
Figure 1. Dependence of the concentrations of the different products of methane decomposition, the temperature and the rate of flow on the time of the process $(1 - CH_4, \ 2 - C_2H_4, \ 3 - C_2H_2, \ 4 - C, \ 5 - H_2, \ 6 - T, \ 7 - v)$.

$$\frac{dC_2}{dx} = \frac{1}{v}\frac{M_2}{M_1}k_1^\star C_1 + \frac{AN_A}{v^2}\left(\frac{M_2}{M_1 M_3}k_2^\star C_1 C_3 - \frac{2}{M_2}k_3 C_2^2 - \right.$$
$$-\frac{1}{M_5}k_5 C_2 C_5 - \frac{1}{M_6}k_7 C_2 C_6 - \frac{1}{M_7}k_9 C_2 C_7 - $$
$$-\frac{1}{M_8}k_{11}C_2 C_8 + \frac{M_2}{M_1 M_6}k_{12}^\star C_1 C_6 + \frac{M_2}{M_1 M_8}k_{13}^\star C_1 C_8 - $$
$$\left.-\frac{1}{M_9}k_{15}C_2 C_9\right) \tag{35}$$

$$\frac{dC_3}{dx} = \frac{1}{v}\frac{M_3}{M_1}k_1^\star C_1 - \frac{AN_A}{v^2}\left(\frac{1}{M_1}k_2^\star C_1 C_3 + \frac{1}{M_5}k_4 C_3 C_5 + \right.$$
$$+\frac{1}{M_6}k_6 C_3 C_6 + \frac{1}{M_7}k_8 C_3 C_7 + \frac{1}{M_8}k_{10}C_3 C_8 + $$
$$\left.+\frac{1}{M_9}k_{14}C_3 C_9\right) \tag{36}$$

$$\frac{dC_4}{dx} = \frac{AN_A}{v^2}\left(\frac{M_4}{M_1 M_3}k_2^\star C_1 C_3 + \frac{M_4}{M_3 M_5}k_4 C_3 C_5 + \frac{M_4}{M_3 M_6}k_6 C_3 C_6 + \right.$$
$$\left.+\frac{M_4}{M_3 M_7}k_8 C_3 C_7 + \frac{M_4}{M_3 M_8}k_{10}C_3 C_8\right) \tag{37}$$

$$\frac{dC_5}{dx} = \frac{AN_A}{v^2}\left(\frac{M_5}{M_2^2}k_3 C_2^2 - \frac{1}{M_3}k_4 C_3 C_5 - \frac{1}{M_2}k_5 C_2 C_5 + \frac{M_5}{M_1 M_6}k_{12}^\star C_1 C_6\right) \tag{38}$$

$$\frac{dC_6}{dx} = \frac{AN_A}{v^2}\left(\frac{M_6}{M_3 M_5}k_4 C_3 C_5 + \frac{M_6}{M_2 M_5}k_5 C_2 C_5 - \frac{1}{M_3}k_6 C_3 C_6 - \right.$$
$$\left.-\frac{1}{M_2}k_7 C_2 C_6 - \frac{1}{M_1}k_{12}^\star C_1 C_6\right) \tag{39}$$

$$\frac{dC_7}{dx} = \frac{AN_A}{v^2}\left(\frac{M_7}{M_3 M_6}k_6 C_3 C_6 + \frac{M_7}{M_2 M_6}k_7 C_2 C_6 - \frac{1}{M_3}k_8 C_3 C_7 - \right.$$
$$\left.-\frac{1}{M_2}k_9 C_2 C_7 + \frac{M_7}{M_1 M_8}k_{13}^\star C_1 C_8\right) \tag{40}$$

$$\frac{dC_8}{dx} = \frac{AN_A}{v^2} \left(\frac{M_8}{M_3 M_7} k_8 C_3 C_7 + \frac{M_8}{M_2 M_7} k_9 C_2 C_7 - \frac{1}{M_3} k_{10} C_3 C_8 - \right.$$
$$\left. -\frac{1}{M_2} k_{11} C_2 C_8 - \frac{1}{M_1} k_{13}^\star C_1 C_8 + \frac{M_8}{M_3 M_9} k_{14} C_3 C_9 \right) \tag{41}$$

$$\frac{dC_9}{dx} = \frac{AN_A}{v^2} \left(\frac{M_9}{M_3 M_8} k_{10} C_3 C_8 + \frac{M_9}{M_2 M_8} k_{11} C_2 C_8 - \frac{1}{M_3} k_{14} C_3 C_9 - \right.$$
$$\left. -\frac{1}{M_2} k_{15} C_2 C_9 \right) \tag{42}$$

$$\frac{dC_{10}}{dx} = \frac{AN_A}{v^2} \frac{M_{10}}{M_2 M_9} k_{15} C_2 C_9 \tag{43}$$

$$\frac{dv}{dx} = \frac{R \frac{dT_0}{dx} \sum_{i=1}^{10} \frac{C_i}{M_i} - RT_0 \sum_{i=1}^{10} \frac{1}{M_i} \frac{dC_i}{dx}}{\frac{B}{A} - 2v} \tag{44}$$

$$\frac{d}{dx} \left[A \left(\varepsilon_t + \frac{p}{\rho} + \frac{v^2}{2} + \varepsilon_v \right) \right] =$$

$$= \frac{1}{v} \left(k_{ev} \frac{C_1}{M_1} n_e \hbar \omega_{II} - k_1^\star \frac{C_1}{M_1} \Delta H_1 \right) - \frac{AN_A}{v^2} \left(k_2^\star \frac{C_1 C_3}{M_1 M_3} \Delta H_2 + \right.$$

$$+k_3 \left(\frac{C_2}{M_2} \right)^2 \Delta H_3 + k_4 \frac{C_3 C_5}{M_3 M_5} \Delta H_4 + k_5 \frac{C_2 C_5}{M_2 M_5} \Delta H_5 +$$

$$+k_6 \frac{C_3 C_6}{M_3 M_6} \Delta H_6 + k_7 \frac{C_2 C_6}{M_2 M_6} \Delta H_7 + k_8 \frac{C_3 C_7}{M_3 M_7} \Delta H_8 +$$

$$+k_9 \frac{C_2 C_7}{M_2 M_7} \Delta H_9 + k_{10} \frac{C_3 C_8}{M_3 M_8} \Delta H_{10} + k_{11} \frac{C_2 C_8}{M_2 M_8} \Delta H_{11} +$$

$$+k_{12}^\star \frac{C_1 C_6}{M_1 M_6} \Delta H_{12} + k_{13}^\star \frac{C_1 C_8}{M_1 M_8} \Delta H_{13} + k_{14} \frac{C_3 C_9}{M_3 M_9} \Delta H_{14} +$$

$$\left. +k_{15} \frac{C_2 C_9}{M_2 M_9} \Delta H_{15} \right) \tag{45}$$

We add the relation of vibrational and translational temperatures to Equations (34-45):

$$T_v = aT_0, \tag{46}$$

where the coefficient $a = 1.1, \ 1.2, \ 1.3$. In Equations (34-46) $C_1 - C_{10}$ are weight fractions of substances CH_4, CH_3, H , H_2, C_2H_6, C_2H_5, C_2H_3, C_2H_4, C_2H_2 and H_5, which according to (33) may exist in gas mixture; $M_1 - M_{10}$ are molecular weights of these substances, and $k_1^* - k_{15}$ are rate constants of reactions (33). Equations (34-46) with initial conditions, peculiar for supersonic plasmachemical discharges

$$P(0) = 0.1 \text{ atm}, \quad T(0) = 3 \cdot 10^2 \text{ K}, \quad v(0) = 3 \cdot 10^5 \text{ cm/s}$$
$$C_1(0) = 1, \quad C_2(0) = C_2(0) = ... = C_{10}(0) = 0,$$

are a kind of Cauchy problem for the system of nonlinear ordinary differential equations of first order for concentrations and temperatures.

The solution for the rate constants were obtained [15]:

$$k_1^* = 10^{15.3} \exp\left\{-\frac{104 \cdot 10^3}{R_0 T_v}\right\}$$

$$k_2^* = 10^{11.1} \exp\left\{-\frac{12.6 \cdot 10^3}{R_0\left[T_0(1-\alpha) + T_v\alpha\right]}\right\}, \quad \alpha = 0.5$$

$$k_3 = 10^{10.7}, \quad k_4 = 10^{11.1} \exp\left\{-\frac{9.7 \cdot 10^3}{R_0 T_0}\right\}$$

$$k_5 = 10^{8.8} \exp\left\{-\frac{11.6 \cdot 10^3}{R_0 T_0}\right\}, \quad k_6 = 10^{9.2}$$

$$k_7 = 10^{8.4}, \quad k_8 = 10^{9.9} \exp\left\{-\frac{7.2 \cdot 10^3}{R_0 T_0}\right\}$$

$$k_9 = 10^{8.6} \exp\left\{-\frac{11 \cdot 10^3}{R_0 T_0}\right\}, \quad k_{10} = 10^{14.6} \exp\left\{-\frac{47.3 \cdot 10^3}{R_0 T_0}\right\}$$

$$k_{11} = 10^9, \quad k_{12}^* = 10^8 \exp\left\{-\frac{11 \cdot 10^3}{R_0\left[T_0(1-\alpha) + T_v\alpha\right]}\right\}, \quad \alpha = 0.3$$

$$k_{13}^* = 10^9 \exp\left\{-\frac{20 \cdot 10^3}{R_0\left[T_0(1-\alpha) + T_v\alpha\right]}\right\}, \quad \alpha = 0.3$$

$$k_{14} = 10^{10.6} \exp\left\{-\frac{1.3 \cdot 10^3}{R_0 T_0}\right\}, \quad k_{15} = 10^{7.4} \exp\left\{-\frac{7.7 \cdot 10^3}{R_0 T_0}\right\}.$$

The results of calculations of plasmachemical conversion of methane into acetylene are shown in Figure 2 and Figure 3. Figure 2 shows the dependence of the acetylene concentration C_2H_2 on the specific energy E_d introduced in the system at three selected pressures. Figure 3 shows the dependence of the energy E_e needed for acetylene production on energy E_d at various degrees of gas nonequilibrium states.
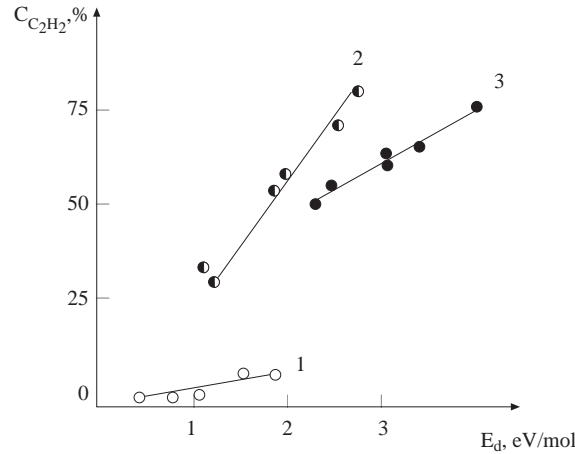
Figure 2. Dependence of the acetylene concentration $C_{C_2H_2}$ on the specific energy E_d introduced in the system at three pressures.

1. $p = 0.01$ atm
2. $p = 0.1$ atm
3. $p = 1$ atm
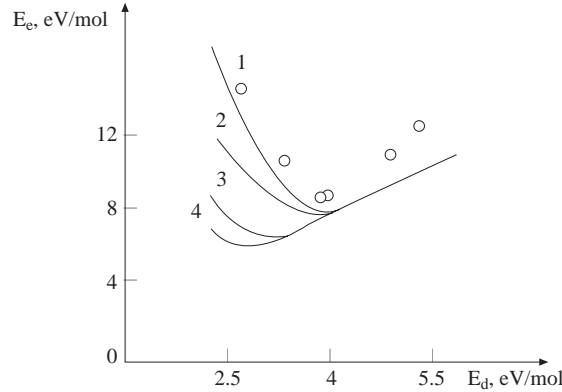
Figure 3. Dependence of energy E_e needed for acetylene production on the energy E_d introduced in the system at various degrees of gas nonequilibrium states.

1. $a = 1$ (calculation for quasiequilibrium process)
2. $a = 1.3$ (calculation for nonequilibrium process)
3. $a = 1.5$ (calculation for nonequilibrium process)

The mathematical modeling of the process shows that:

1. Conversion process proceeds from two temperature regimes. (I) $T = 2000 - 4000$ K "hot" regime; corresponding to conversion conditions in the arc discharge. It requires the forced hardening of reaction products. (II) $T = 1600 - 2000$ K "cold" regime; corresponding to conversion conditions in radio frequency discharge. It does not require the forced hardening of reaction products.

2. Optimal conditions for methane conversion into acetylene are: $p = 0.1$ atm; $a = 1.5$; $T_0 = 1600$ K, $T_v = 2400$ K; $E_d = 2.8$ eV/mol CH_4; $E_e = 6$ eV/mol C_2H_2. Under these conditions the methane conversion reaches 80%. A comparison of calculated results with experimental data shows that time 10^{-4} - $10^{-3}s$ reproduce all main peculiarites of calculated curves.

4. Conclusions

1. The mechanism and kinetics of natural gas dissociation in quasiequilibrium and nonequilibrium conditions were studied. The optimal conditions for methane into acetylene conversion were found.

2. The investigation of quasiequilibrium and nonequilibrium systems showed that the most energy efficiency of plasmachemical processes is obtained in nonequilibrium conditions, especially, where stimulated by vibrational excitation of molecules.

3. It is shown, that optimal conditions for nonequilibrium reactions may be obtained in supersonic flows of plasma.

4. The results of mathematical calculations were compared with experimental results. The good coincidence of results shows the correctness of the mathematical model and its promising use in future investigations.

Appendix

To find the rate of the plasma flow v, we use the Equations (1)-(5). To take the integral of Equations (1), (3) and (5), we rewrite Equations (1)-(5) as:

$$\rho v = A \tag{47}$$

$$\frac{dC_i}{dx} = \frac{m_i}{A} k_i, \quad C_i = \frac{m_i n_i v}{A} = \frac{\rho_i}{\rho} \tag{48}$$

$$Av + p = B \tag{49}$$

$$A(U + \frac{p}{\rho} + \frac{v^2}{2}) = L \tag{50}$$

$$p = \frac{\rho RT}{M} = \rho RT \sum_{i=1}^{5} \frac{C_i}{M_i} = \frac{A}{v} RT \sum_{i=1}^{5} \frac{C_i}{M_i}, \tag{51}$$

where A, B and L are the constants of the integration. In Equations (1), (3) and (5) dissipative terms, including the diffusion, the viscosity and the heat conduction, are neglected.

Substituting for p from (51) into (49), yields

$$v^2 + RT \sum_{i=1}^{5} \frac{C_i}{M_i} - \frac{B}{A} v = 0 \tag{52}$$

$$v = \frac{1}{2} \frac{B}{A} - \sqrt{\left(\frac{1}{2} \frac{B}{A}\right)^2 - RT \sum_{i=1}^{5} \frac{C_i}{M_i}}. \tag{53}$$

In (50) the expression

$$U + \frac{p}{\rho} = H = \frac{1}{\rho} \sum_{i=1}^{5} m_i n_i H_i = \sum_{i=1}^{5} C_i H_i \tag{54}$$

is the enthalpy of the mass unit of the gas, and

$$H_i = \sum_{j=1}^{8} h_{ij} T^j + h_i^0 \tag{55}$$

is the enthalpy of the mass unit of the i th component of the gas.

To get dT/dx we differentiate (50) and (52) with respect to x. Thus we obtain (26) after a little rearrangement.

Equations (21) - (25) were obtained from (6) in accordance with scheme (17) - (20), and suggested by Cassel:

$$
\begin{aligned}
K_1 &= -k_1 n_1 \\
K_2 &= \frac{1}{2} k_1 n_1 - k_2 n_2 \\
K_3 &= k_2 n_2 - k_3 n_3 \\
K_4 &= 2 k_3 n_3 \\
K_5 &= k_1 n_1 + k_2 n_2 + k_3 n_3.
\end{aligned}
$$

In the same manner (34)-(44) were obtained in accordance with scheme (33).

Equation (45) is the equation of the total energy, in which the left side is

$$\varepsilon_t + \frac{p}{\rho} + \frac{v^2}{2} = \beta \frac{RT_0}{M} + \frac{v^2}{2}$$

and

$$\varepsilon_v = R \frac{C_1}{M_1} \sum_{j=1}^{3} \frac{\frac{\hbar \omega_j}{R}}{\exp\left\{\frac{\hbar \omega_j}{RT_v} - 1\right\}}.$$

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Here,

$$\beta = \frac{\gamma}{\gamma - 1}, \quad \gamma = \frac{C_p}{C_v}$$

is the ratio of the heat capacities, and j is the type of the vibration of the molecule.

The right side of (45) is (see Equations (11)-(16)):

$$
\begin{aligned}
\varepsilon_{eV} - (1 - \alpha)\varepsilon_R &= k_{ev}n_e n\hbar\omega_{II} - (1 - \alpha)k_r n^2 \Delta Q \\
&= k_{ev}n_e n\hbar\omega_{II} - \Delta H k_\tau n^2,
\end{aligned}
$$

where ΔH is the heat effect of the reaction.

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