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Abstract

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SOME QUESTIONS OF THE KINETICS OF CHEMICAL REACTIONS IN PLASMA JETS

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Recently, high-temperature ($T = 10^3$—10^4 K) chemical reactions occurring in plasma jets have acquired great theoretical and applied importance. The study of reactions of this type and their application in industry is the subject of a new field of physical chemistry, which may be called plasma chemistry. The scientific and theoretical foundations of plasma chemistry have not yet been established, which makes it difficult to formulate scientifically grounded recommendations for the calculation and design of experimental and industrial installations. The main problems that must be solved in establishing the foundations of the kinetics of plasma-chemical reactions are: a) questions of Maxwellization in a plasma jet; b) the influence of turbulent mixing and collective processes on the rates of reactions in the jet; c) the question of how and to what extent the Arrhenius equation should be modified when describing reactions occurring under high-temperature conditions; d) the problem of the mechanism of cooling (quenching) of a plasma jet during reaction by the reacting substances (autostabilization of plasma-chemical reactions) in the corresponding space-time intervals, with rates sufficient for fixing the products of high-temperature chemical processes; e) the question of the effective dimensions of plasma-chemical reactors; f) questions of controlling plasma-chemical reactions.

In the present work, apparently for the first time, an attempt is made to consider theoretically a number of general kinetic questions of plasma-chemical reactions, to elucidate one of the possible mechanisms of quenching a plasma jet by reacting substances, and to estimate the dimensions of the reactor. The consideration is carried out using the following model. Into a cylindrical tube of diameter d_0, through an inlet channel (nozzle) of diameter $d < d_0$, a plasma jet with initial substances A is introduced. The initial gas velocity v_A, which is less than the speed of sound (Mach number ≈ 0.2—0.5), and the initial temperature T_A and pressure P_A do not change with time. The temperature T_A considerably exceeds all thermal thresholds of the reactions of interest to us. In some cross section of the tube at a distance z_0 from the inlet channel, on the surface of the tube there are n openings of diameter $\delta \ll d < d_0$. Through these openings, in a direction perpendicular to the flow of gas A, a liquid B is supplied under considerable pressure at a constant velocity $v_B \ll v_A$. The liquid B and gas A may consist of several components, representing the initial substances necessary for obtaining the desired products. It is assumed that upon contact of substances A and B the following processes occur: heating and evaporation of liquid B, its dissociation, chemical reactions leading to the formation of the desired products, and decomposition reactions of the desired products. The kinetics of reactions in a plasma jet has a number of special features. 1) The reactions proceed mainly over a relatively small section of the tube of length l, hereinafter called the reactor; the dimensions of the reactor are unknown and are determined by the geometrical configuration of the installation and by the kinetics of the processes occurring in it. 2) The reactor is an open system, since continuous material exchange takes place through its boundaries. 3) Reactions in a plasma jet are nonisothermal reactions. 4) Nonisothermal conditions in the reactor arise in the course of the "target" reaction and the physicochemical processes accompanying it, and are determined by the kinetics of these processes. 5) The initial temperature in the reactor is high, and therefore the rate of temperature decrease—

the temperature in the reactor must be very high, for otherwise the target products will have time to decompose. b) In a plasma jet both homogeneous processes and heterogeneous processes (at the liquid—gas interface) take place.

A number of hydrodynamic factors affect the physicochemical processes in a plasma jet.

1. Under the dynamic action of the gas flow, liquid jets break up into a multitude of drops of various sizes, changing the effective reaction surface of the liquid and the distribution of the liquid in the plasma jet.
2. The rate of reactions in a plasma jet is also influenced by the character of the flow of the hot gas in the reactor, since it affects the values of the transfer coefficients, the rate of energy dissipation, and the geometrical configuration of the jet.

In the present work the following method is proposed for calculating the quenching rate of a plasma jet, making it possible to avoid the difficulties associated with a detailed consideration of the kinetics of reactions that have been insufficiently studied in a plasma jet. The general energy balance of the liquid—gas system is considered. Gas molecules, continuously bombarding the surface of the liquid, transfer to it a certain energy, which is expended in the processes occurring on the liquid surface. The liquid surface, with respect to the gas, may be regarded as a negative source (sink) of heat. To calculate the rate of decrease of the gas temperature, the heat-transfer equation with negative heat sources is used. The volume density of heat sinks $Q(z)$ (i.e., the energy transferred to the liquid per unit time from a unit volume of gas) is estimated by means of the methods of statistical physics and kinetics. It should be emphasized that a quantitative description of nonisothermal reactions, as is known ([1,2]), leads to partial differential equations which, in the general case, are not solved.

The hydrodynamic factors noted above, and the fact that a plasma-chemical reactor is an open system, further complicate the problem to a considerable extent. From what has been said it is clear that the quantitative description of reactions in a plasma jet is a rather complex problem, in considering which one has to be satisfied only with approximate solutions, which can claim only to reflect qualitatively correctly the principal features of the phenomena considered and to give the correct orders of magnitude.

Let us first briefly consider the necessary hydrodynamic questions. Proceeding from the theory of the atomization of liquid jets in a gas ([3]), it can be shown that in a time (representing its upper bound)

$$\tau_p \approx \sqrt{\delta^2 \rho_A / 4 v_A^2 \rho_B}$$

a liquid jet B, entering the plasma jet, breaks up into a multitude of drops of different sizes, which may roughly be divided into small and large drops with mean radii equal, respectively, to

$$L_k \approx (3 \div 5)\delta, \qquad L_m \approx \frac{\alpha}{\rho_A v_A^2} \ll L_k, \tag{1}$$

where α is the surface tension of the liquid, and ρ_A and ρ_B are, respectively, the densities of the gas and the liquid. The role of the large drops is relatively small, since they are few in number and they have a comparatively small surface; moreover, they continue to disintegrate. Therefore we shall base our estimates on the consideration of small drops. The liquid drops formed execute a complex motion in the gas flow, which may be decomposed into two components: a) retarded motion by inertia perpendicular to the gas flow with velocity $v_\perp(t)$; b) accelerated motion along the tube axis under the influence of the plasma jet with velocity $v_\parallel(t)$. It can be shown that, for small drops, Stokes' formula ([4]) is applicable as the laws of braking in the direction perpendicular to the gas flow and of acceleration in the longitudinal direction, leading to the following laws of variation of the velocities of drop motion.

relative to the tube with time t:

$$v_\perp(t) \simeq v_\mathrm{B} \exp\left(-\frac{t}{t_0}\right), \qquad v_\parallel(t) \simeq v_\mathrm{A}\left[1 - \exp\left(-\frac{t}{t_0}\right)\right], \qquad t_0 \simeq \frac{L_\mathrm{m}^2 \rho_\mathrm{B}}{4.5 \nu \rho_\mathrm{A}}, \tag{2}$$

where ν is the kinematic viscosity of the gas. It follows from formulas (2) that, under steady-state conditions, the droplets are initially distributed along the periphery in the plasma jet and then approach its axis. The number of droplets formed per unit time can be estimated from the formulas

$$\frac{dN_\mathrm{m}}{dt} \simeq \frac{\eta}{\frac{4\pi}{3} L_\mathrm{m}^3} \frac{dV}{dt}, \qquad \frac{dV}{dt} = \frac{\pi \delta^2}{4} v_\mathrm{B} n, \tag{3}$$

where dV/dt denotes the volume of liquid B fed per unit time into the reactor, and $\eta \simeq 1$ is the fraction of the liquid atomized in the form of small droplets.

The steady-state surface area of the droplets per unit volume is equal to

$$S_{0\mathrm{m}} \simeq 4\pi L_{\mathrm{m}}^2 N_{0\mathrm{m}} \simeq \eta \frac{\pi\delta^2 v_{\mathrm{B}} v_{\mathrm{A}} \rho_{\mathrm{A}} n}{d^2\alpha}, \qquad N_{0\mathrm{m}} \simeq \frac{1}{d^2 v_{\mathrm{A}}} \frac{dN_{\mathrm{m}}}{dt}. \tag{4}$$

It can also be shown that the plasma jet in the reactor is turbulized to a considerable degree, and therefore the transport coefficients in it exceed the molecular coefficients, which in the hot plasma jet are also very large ([5,6]). To estimate the cooling rate of the plasma jet, let us use the equation of heat transfer in cylindrical coordinates z, r, and φ in the laboratory coordinate system (where $\partial T/\partial t = 0$):

$$c_p \rho v_{\mathrm{A}} \frac{\partial T}{\partial z} = \chi \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) - Q(z) - \theta - \theta_1(z), \tag{5}$$

where the dependence of the thermal conductivity of the gas χ on z and r is not taken into account; θ is the energy dissipated in the gas owing to viscosity and turbulence and lost through heat transfer through the tube walls, and $\theta_1(z)$ is that carried away by radiation; $Q(z)$ is the energy absorbed from a unit volume of gas per unit time at the surface of the liquid; ρ is the gas density; c_p is the heat capacity per unit mass at $p = \text{const}$; the z axis is directed along the axis of the tube. In the case under consideration the following conditions are satisfied: $v_{\mathrm{A}} l \gg \chi$, $d_0^2 v_{\mathrm{A}}/l \gg \chi$, $Q(z) \gg \theta$, $\theta_1(z) < Q(z)$, where χ is the thermal diffusivity of the gas. These conditions make it possible to rewrite equation (5) in the following simplified form:

$$c_p \rho v_{\mathrm{A}} \frac{\partial T}{\partial z} = -Q(z). \tag{6}$$

Let us estimate the quantity $Q(z)$. In doing so we shall proceed from the Maxwellian distribution of gas molecules over velocities.* Then the energy transferred to the liquid by gas molecules that strike the surface of droplets located in a gas volume element ΔV is equal to $\Delta E = \omega\varepsilon_0 S_{0\mathrm{m}} \Delta V/b$, where $\varepsilon_0 = P\sqrt{kT/\pi m}$ is the kinetic energy of gas molecules striking a unit surface per unit time ([8]); ω is the fraction of energy transferred by gas molecules to the surface of the liquid; P is the pressure; m is the averaged mass of a gas molecule; $b < 1$ is a quantity reflecting the nonuniformity of the distribution of droplets over the jet cross section. Then the required volume density of negative heat sources can be estimated by the formula**

$$Q(z) = \frac{\Delta E}{b\Delta V} = \eta\omega \frac{\delta^2 v_{\mathrm{A}}^2 v_{\mathrm{B}} \rho_{\mathrm{A}} n P}{b\,\alpha d^2} \sqrt{\frac{kT}{m}}, \tag{7}$$

where ρ and T are functions of z. From (8) and (9) we obtain the magnitude of the gradient

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* In view of the fact that the mean speed of thermal motion is several times greater than the speed v_{A}, the number of impacts of gas molecules on the surface of the droplets will differ little from the number of impacts in a stationary gas ([7]).

** It should be noted that, because of the low thermal diffusivity of the liquid χ_{B}, the time $t_{\mathrm{B}} \simeq L_{\mathrm{m}}^2/\chi$ required for heating a liquid droplet is large in comparison with the time

temperature along the z axis in the laboratory coordinate system

$$\frac{\partial T}{\partial z} = -\frac{Q(z)}{c_p \rho v_A} \approx \eta\omega \frac{\delta^2 v_B n P}{bad'^2 c_p} \sqrt{\frac{kT}{m}}. \tag{8}$$

The rate of change of temperature in a moving gas element is determined by the formula

$$\frac{\partial T}{\partial t} = v_A \frac{\partial T}{\partial z} = \eta\omega \frac{v_A \delta^2 v_B n P}{bad'^2 c_p} \sqrt{\frac{kT}{m}}. \tag{9}$$

As the dimensions of the reactor we choose the section of tube over which the temperature of the plasma jet falls from T_A to a prescribed value T_f, for example to that below which the rate of decomposition of the desired reaction products becomes negligibly small. Analytically the reactor length l is determined by the expression

$$T_A - T_f = \int_0^l \frac{\partial T}{\partial z}\, dz = \left(\frac{\partial T}{\partial z}\right)^* l; \qquad l = \frac{T_A - T_f}{(\partial T/\partial z)^*}, \tag{10}$$

where $(\partial T/\partial z)^*$ is some intermediate value of the quantity $\partial T/\partial z$, obtained in accordance with the mean-value theorem [9].

In formulas (8)–(10) the quantities on the right are known or can be estimated. This makes it possible to find $\partial T/\partial z$, $\partial T/\partial t$, and l. Taking the values $T = 6 \cdot 10^3$°K, $m \approx 2 \cdot 10^{-23}$ g; $n = 6$; $\delta = 2 \cdot 10^{-2}$ cm; $d' = 0.5$ cm; $\alpha = 70$ erg/cm^2; $\mu = 20$; $\rho_B = 1$ g/cm^3, we obtain $\partial T/\partial z = 10^3 \eta\omega/b$ deg/cm; $\partial T/\partial t \approx 4 \cdot 10^7 \eta\omega/b$ deg/sec. If it is assumed that $T_A - T_f \approx 10^3$°K, then $l \approx 1$ cm, $\tau_A \approx l/v_A \approx 10^{-5}$ sec. The obtained relations and estimates show that the mechanism of cooling of a plasma jet in the state proposed in the present note provides sufficiently rapid quenching. The relations found also indicate ways of accelerating quenching. Formulas (10) show that in the plasma jet the reactions proceed effectively only over a very small section of the tube. Therefore reactions in a plasmatron, in particular "quenching," can be effectively influenced only over this small section of the tube.

Let us note that taking into account the terms θ and $\theta_1(z)$, which we discarded in equations (5) and (6), as well as the influence of large droplets, can lead only to an increase in the calculated quenching rate and a decrease in the reactor dimensions. Therefore the formulas obtained give estimates for the lower bound of the rate and cooling of the plasma jet and the upper bound of the reactor dimensions.

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t_0 of its motion in the reactor. Therefore it may be considered that evaporation of the liquid occurs only from the surface. Moreover, usually the heat of evaporation of the liquid λ is close to the mean kinetic energy of the molecules of the plasma jet (for example, $\lambda \approx 10$ kcal/mole, while at $T = 6 \cdot 10^3$°K, $RT \approx 10$ kcal/mole). Therefore it should be expected that the impacts of the gas molecules against the surface of the liquid will be highly effective, so that $\omega \simeq 1$. The time necessary for complete evaporation of a droplet, equal to $\tau_d \approx \lambda \rho_B L_M / \omega \varepsilon_0$, substantially exceeds t_0. Therefore it should be considered that in the reactor the liquid passes into the gaseous state only partially. Let us also note that the described approach to evaporation of liquid droplets can be applied without substantial changes to the problem of evaporation (sublimation) of a solid phase fed into the plasma jet in the form of fine particles. In this case one should take into account not only evaporation of the body, but also its melting.

Note: Figure translations are in progress. See original paper for figures.