KINETICS OF CHEMICAL REACTIONS IN LOW-TEMPERATURE PLASMA JETS

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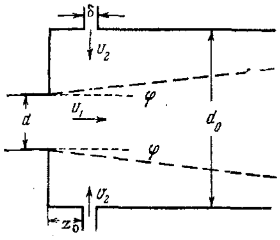
The question of high-temperature chemical reactions in plasma jets at jet temperatures of the order of 10^3–$10^{4\circ}$ K has recently become the subject of intense study.* These reactions and their applications are, in fact, a new branch of physical chemistry which might be described as plasma chemistry, a border discipline with elements of chemistry, physics and mechanics, from all of which it borrows ideas and methods. Plasma chemistry may justifiably be regarded as a separate study because of the various characteristic properties of plasmochemical reactions. However, it still lacks a proper scientific basis and the provision of such a basis should be one of the immediate concerns of the plasma chemist.

The question of the kinetics of plasmochemical reactions was apparently first raised and studied in [1]. The present paper forms a continuation of that work.

One of the problems of plasma chemistry is the problem of creating the conditions for very rapid cooling of the plasma jet in the course of the reaction (self-cooling) or forced cooling at certain space-time intervals, which is necessary to preserve the target products. The study of this question has raised various problems of the hydrodynamics of high-temperature jets and the related heat transfer processes. This paper examines one of the possible mechanisms of self-cooling in a plasma jet. The principal plasmochemical processes are confined to a relatively small part of the jet of length l, which will be referred to as the reactor. Below, a method of estimating the effect dimensions of the reactor, which are unknown, is proposed and various parameters of the reactor processes are determined.

§1. Some properties of the kinetics of reactions in a plasma jet. Consider the following model (see figure). A plasma jet A enters a cylindrical pipe of diameter d_0 through an inlet duct (nozzle) of diameter $d < d_0$ at a constant velocity v_{01} less than the speed of sound (Mach number $M \approx 0.2$–0.5). The temperature T_{01} and pressure p_0 of the gas at the inlet do not vary with time.



In a certain section of the pipe perpendicular to its axis and at a distance z_0 from the nozzle exit (see figure) there are n openings of diameter $\delta \ll d_0$ in the surface of the pipe. Through these openings at a constant considerable pressure and fixed velocity $v_{02} \ll v_{01}$ there is fed a low-viscosity liquid B, such as water, at temperature T_{02}. Moreover, $v_{02} \perp v_{01}$. We assume that when substances A and B meet the following processes are possible: 1) heating of liquid B from temperature T_{02} to temperature T_3 at which the liquid boils and evaporates; 2) evaporation of liquid B at temperature T_3; 3) dissociation of substance B; 4) heating of the vapor of substance B and the products of the reactions proceeding at the surface of the liquid to the variable temperature T_1 of the gas mixture; 5) chemical reactions leading to formation of the target product; 6) decomposition of the target reaction products. The kinetics of plasma jet processes possess a number of specific properties.

First, the reactions in the plasma jet proceed mainly within a relatively short segment of the pipe of unknown length l, which must be determined; second, the reactor is an open system; third, the reactions in the plasma jet are nonisothermal; fourth, in the case in question nonisothermal conditions are not created in the reactor by external factors, but arise mainly in the course of the physicochemical processes that take place in it and are determined by their kinetics; fifth, the initial temperature T_{01} of the plasma jet corresponds to a very high rate of the chemical reactions in it; therefore, to prevent total decomposition of the target products, extremely high rates of cooling must be provided in specific parts of the reactor; sixth, both homo- and heterophase (at the liquid-gas interface) processes occur in the plasma jet. In addition, it is also necessary to take into account the influence of a number of hydrodynamic factors.

1. The hydrodynamic action of the gas stream causes the jets of liquid to break down into a multitude of drops of various dimensions. This reacts on the kinetics of the reaction processes mainly in two ways: a) it changes the effective surface area of the liquid; b) the drops of liquid are entrained by the gas flow, which affects the distribution of liquid in the plasma jet.

2. The degree of turbulence of the gas flow in the reactor has an effect on the transport coefficients, the rate of energy dissipation, the configuration of the jet, and so on.

3. The change in gas temperature leads to a change in the rate of flow v_1 and kinematic viscosity ν, and hence to a change in the Reynolds number R. It follows from the above that the construction of an exact quantitative theory of plasma jet reactions is a very complex problem, and for the time being we must rest content with approximate solutions and relations that can claim only to give a reliable qualitative reflection of the main features of the phenomena and the correct order of magnitude of the quantities.

§2. Some laws of atomization and disintegration of liquid jets in a plasma jet. The jet of liquid B entering the gas flow A is subjected to the dynamic action of this flow. This action varies in degree according to the relative velocity v_{12} of the liquid and the gas. Since

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*At these temperatures in the absence of external electric and magnetic fields it is usual to neglect electromagnetic processes.

usually $v_1 \gg v_2$, we may assume that $v_{12} \approx v_1$; it is considered that the condition

$$\frac{\rho_1 v_1^2}{2} \gg \frac{2\alpha}{\delta} \quad \text{or} \quad v_1 > \left(\frac{4\alpha}{\delta\rho_1}\right)^{1/2} \tag{2.1}$$

is satisfied.*

Here ρ_1 is the density of gas A, α is the surface tension of liquid B. It is known that [2] that, at sufficiently high rates of relative motion of the gas and the liquid jet, the jet breaks down under the dynamic action of the gas into a conglomeration of coarse and fine drops. The degree of atomization depends on how long the jet of liquid intersecting the gas stream is subjected to its dynamic action and how this time is related to the time interval required for total atomization. At present, we are not in a position to offer rigorous quantitative answers to these questions, since we lack a developed quantitative theory of the corresponding hydrodynamics. However, we can make certain estimates that throw some light on the qualitative aspects of the phenomena involved. In this connection, we make use of the results of [2]. The general qualitative picture of the disintegration of the jet is as follows: perturbations at the surface of the jet produce short and long (as compared with $\delta/2$) waves.

The instability of the short waves leads to the detachment of fine drops of radius $L_1 \ll \delta/2$, while the instability of the long waves causes the jet to break up into coarse drops of radius $L_2 \approx (3-5)\,\delta$. The time required for total atomization and disintegration of the jet of liquid B and the length L of the continuous (intact) part can be estimated as

$$\tau \approx \frac{\delta}{2v_1}\left(\frac{\rho_2}{\rho_1}\right)^{1/2}, \qquad L \approx \tau v_2, \qquad \rho_2 \gg \rho_1 \,. \tag{2.2}$$

If $L \ll d'$ (where d' is the diameter of the gas stream), then the jet of liquid is almost completely broken up into drops of various sizes. If, however, $L \gg d'$, then the jet will succeed in crossing the gas stream almost intact. Disintegration of the jet results in the formation of drops of various dimensions. However, at present we are still apparently unable to determine the drop size distribution function. Roughly speaking, we can divide all the drops into fine and coarse and estimate their respective mean sizes from the formulas [2]

$$L_1 \approx \frac{\alpha}{\rho_1 v_1^2}, \qquad L_2 \approx (3-5)\,\delta \,. \tag{2.3}$$

The above considerations are based on the assumption that the jet disintegrates owing to the presence at its surface of infinitely small perturbations [2]. In fact, jets of liquid B are subjected to the action not of infinitely small, but of finite and even perhaps considerable perturbations, the more so in that the same jets are also subjected to specific perturbations resulting from the fact that the liquid and the gas flow in mutually perpendicular directions. These perturbations lead to the disintegration of the jet in a time shorter than that calculated from (2.2). In this case the disintegration time will depend on the specific form of the perturbations and will scarcely be amenable to exact calculation. It follows that the values of τ and L computed from (2.2) are their greatest possible values.

§3. Motion of drops formed upon disintegration of a liquid jet in a gas flow. The depth of penetration of the drops of liquid into the gas stream and their distribution in the gas are mainly determined by the following factors: a) the retardation of the transverse motion of the drops in the gas stream and the length of the path traveled by the drops in a direction perpendicular to the gas stream; b) the acceleration of the drops in the direction of the gas stream and the length of the path traveled by the drops along the axis of the pipe; c) the possible effect of the turbulent nature of the gas flow on the motion of drops suspended in the gas stream; d) the rate of evaporation of the liquid and the time required for total conversion of the liquid to vapor. All these effects are discussed below.

In considering the laws of motion of drops of liquid in a plasma jet it is impossible completely to disregard the fact that the gas temperature is quite high, since this affects the Reynolds number and hence the structure of the equations of motion of the drops. It is assumed that the density ρ_1 of the gas, the number N of particles in unit volume, the pressure p, and the molecular weight μ of the gas mixture are given by

$$\rho_1 = \frac{\mu p}{RT_1}, \qquad N = \frac{\mu p}{mRT_1}, \tag{3.1}$$

$$\rho_1 = \sum \rho_i, \quad p = \sum_i p_i, \quad \mu = \frac{1}{p}\sum_i p_i \mu_i, \tag{3.2}$$

$$m = \frac{1}{N}\sum_i m_i N_i, \quad N = \sum_i N_i \,.$$

Here the summation is taken over all components of the gas mixture, the partial densities, pressures, molecular weights, numbers of particles in unit volume and molecular masses of which are equal to ρ_i, p_i, μ_i, N_i, m_i.

In view of the fact that $\nu \sim T^{3/2}$ [2], an increase in the temperature of the gas in the plasma jet by a factor of 10–30 as compared with the ordinary temperatures of the cold gas causes, other things being equal, an increase in ν and a decrease in R by a factor of 30–150. Accordingly, the R numbers corresponding to gas flow past fine drops of liquid will be relatively small, which justifies us in assuming that the motion of the drops is Stokesian [4].

The Reynolds number corresponding to the beginning of motion of a fine drop in a direction perpendicular to the gas stream is $R' = v_2 L_1/\nu < 1$, and the (corresponding) equation of motion of the fine drop (which we assume to be spherical) takes the form

$$v_\perp = v_2 \exp(-t/t_0) \qquad (t_0 = L_1^2\rho_2 / 4.5\nu\rho_1)\,. \tag{3.3}$$

From (3.3) it is clear that in the course of a time interval of the order of t_0 the fine drops travel a distance

$$\Delta L_1 = \int_0^{t_0} v_\perp \, dt \approx v_2 t_0 \tag{3.4}$$

in the transverse direction.

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*Note that the effect of the high gas temperature has still not been taken into account. It will be introduced later.

If $(L + \Delta L_1) > d'$, then the liquid can cross the gas stream and reach the opposite wall of the pipe.* Otherwise the drops "get stuck" in the gas flow.

We shall now consider the motion of the fine drops along the pipe axis. The corresponding Reynolds number $R'' = uL_1/\nu$ ($u \leqslant v_1$ is the relative velocity of drop and gas in the longitudinal direction) usually satisfies the condition $R'' \approx 1 \ll R_*$ (R_* is the critical value of R for flow past a sphere); thus we are again able to use the Stokes equation [5] and obtain for the motion of the drop in the longitudinal direction

$$v_{\parallel} = v_1\left[1 - \exp\left(-\frac{t}{t_0}\right)\right], \quad \Delta L_{\parallel} = \int_0^{t_0} v_{\parallel}\, dt \approx \frac{v_1 t_0}{3}. \qquad (3.5)$$

From (3.3) and (3.5) we can obtain the equation of the trajectories of the fine drops in a laboratory coordinate system (assuming that the trajectory of each drop is a plane curve) and also a qualitative picture of the distribution of the fine drops in the plasma jet. Each jet of liquid has a continuous (intact) part (of length $L' = (d_0 - d')/2 + L$), which serves as a source of drops. Initially the drops are located in the peripheral part of the plasma jet. Then, in accordance with (3.3) and (3.5), they penetrate into the gas stream, reach the axis of the pipe, and then form a divergent beam.

The motion of the coarse drops can be considered in much the same way. These drops will have different trajectories, since (as $L_2 \gg L_1$) the corresponding Reynolds numbers will considerably exceed those for the fine drops. However, the qualitative distributions of drops of both sizes will be similar. In our approximation it is sufficient to study the behavior of the fine drops, which obviously make the main contribution to the effective surface of the liquid.

§4. Estimation of the effective surface of the liquid in the plasma jet. The number of fine drops formed in unit time

$$\frac{dn_1}{dt} = \frac{\eta}{{}^4/_3\pi L_1^3}\frac{dV}{dt} \qquad \left(\frac{dV}{dt} = \frac{\pi\delta^2}{4} v_2 n\right). \qquad (4.1)$$

Here η is the fraction of liquid converted into fine drops.

Under steady-state conditions a constant spatial distribution of the drops is established.

The number of drops formed during time Δt is equal to $\Delta n_1 = (dn_1/dt)\Delta t$. These drops are distributed in a volume of gas of the order of $\Delta V = \pi d^{12} v_1 \Delta t/4$. Then the average number of drops in unit volume of the plasma jet and their surface area are

$$n_0 = \frac{\Delta n_1}{\Delta V}, \qquad S_0 = 4\pi L_1^2 n_0 = 2.5\eta \frac{n\delta^2 v_1 v_2 \rho_1}{d'^2 \alpha}. \qquad (4.2)$$

Equations (4.1) and (4.2) relate the rate of formation of drops, their number in unit volume, and the corresponding surface area with the properties of the liquid and the gas, the conditions of supply of liquid and gas to the reactor, and the parameters of the apparatus.*

§5. Nature of gas flow in the plasma jet and transport coefficients. To a considerable extent the kinetics of the reactor processes depend on the nature of the motion of the gas in the reactor.

First, the transport coefficients depend on the degree of turbulence of the gas stream [4, 6]. Second, the diameter of the jet may vary with distance from the nozzle, and the law of variation also depends on the flow regime [4, 7]. Third, at a certain degree of turbulence further disintegration of the drops of liquid (especially the larger ones) is possible as they enter the turbulent flow [2]. Fourth, the motion of drops of liquid in a turbulent flow has a number of characteristic properties [2].

Let us start by considering the degree of turbulence of the gas stream as it leaves the nozzle. For this purpose, we estimate $R = v_1 d/\nu$ for several typical values of v_1, T, and d. As estimates we take $v_1 = 4 \times 10^4$ cm/sec, $d = 0.5$ cm, $p = 1$ atm, and $T = 6 \times 10^{3\circ}$ K. Estimating the kinematic viscosity from the usual formulas [3] ($m = 3 \times 10^{-23}$ g, $\sigma \approx 10^{-15}$ cm^2), we get $\nu \approx 40$ cm^2/sec and $R \approx 500$. Evidently, at these values of R it is possible to assume that the plasma jet leaving the nozzle has quite a considerable degree of turbulence because of the abrupt change of section. In these conditions the laminarity of the flow is disturbed at values of R of the order of 20–50 [2, 4, 5]. The scale of turbulence in the jet leaving the nozzle is of the order of d, and the distance z_0 between the points where gas and liquid are introduced is also of the order of d. Therefore at distances $z_0 \approx d$ the turbulent nature of the gas flow is preserved, and where it meets the liquid jets the plasma jet is quite turbulent. Since the liquid jets constitute an additional obstacle to the flow of gas, the degree of turbulence of the plasma jet is not reduced by its encounter with the liquid.

The subsequent fate of the turbulent jet depends on the Reynolds number $R \approx v_1 d_0/\nu$ corresponding to motion of the gas through a pipe of diameter d_0. It should be borne in mind that on cooling the temperature of the jet over a length l may be reduced by several times and the Reynolds number may change substantially. Hence, in the reactor there is a change in the values of

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*We have still not taken into account the evaporation of the drops or the effect of turbulence of the gas flow on their motion. The possibility of such an approximation is examined below.

*It is assumed that time Δt is not long enough for the drops to evaporate, i.e., $\Delta t < \tau_1$, where τ_1 is the mean drop evaporation time; moreover, it was noted above that the drops are not uniformly distributed over the cross section of the plasma jet. The number defined above gives the number of drops in unit volume that would exist for uniform distribution of the drops over the section of the gas flow.

ν and R from the initial values ν_0, R_0 to the final values ν_f, R_f on leaving the reactor. Two cases are possible:

$$\text{(a)}\, R_f = d_0 v_{1f} / \nu_f < R_*, \qquad \text{(b)}\, R_f > R_* .$$

Here R_* is the critical value of the Reynolds number corresponding to the flow of gas in the pipe after leaving the reactor with velocity v_{1f}.

In this first case the turbulence of the plasma jet will be damped as the gas moves through the pipe, in the second case the turbulence of the plasma jet will not be damped.

Let us now consider the transport coefficients. The thermal diffusivity χ', kinematic viscosity ν', and diffusion coefficient D' in the turbulent flow are given by

$$\chi' = \chi + \chi_1, \quad \nu' = \nu + \nu_1, \quad D' = D + D_1, \quad (\chi_1 \approx \chi R, \; \nu_1 = \nu R, \; D_1 = DR) . \tag{5.1}$$

Here χ, ν, and D are the corresponding molecular transport coefficients in the gas, and χ_1, ν_1, and D_1 the turbulent transport coefficients.

For developed turbulence, the transport coefficients in the plasma jet exceed the molecular coefficients, which in a hot gas jet are themselves quite large.* In this connection it should be noted that the very intense turbulent exchange that takes place in the reactor ensures rapid mixing of the gas and temperature equalization in a direction perpendicular to the gas flow.

§6. Effect of turbulence of the plasma jet on the motion of the drops of liquid and the dimensions of the jet. It is assumed that it is possible to neglect the effect of the drops on the motion of the jet. Drops suspended in the jet may be entrained by the turbulent pulsations and hence describe very complicated trajectories [2]; this entrainment will not be complete since $\rho_2 \gg \rho_1$ [2]. The drop of liquid will be acted upon by turbulent pulsations of different scales. In §3 above it was noted that when a stream of gas flows around a fine drop the corresponding Reynolds numbers are not large and the flow may be regarded as Stokesian. The velocity v_λ of the turbulent pulsations of scale λ does not exceed v_1 [4]. Therefore Stokes law is applicable even in the presence of turbulent pulsations. In this case the velocity increment Δv due to entrainment of the drop by a turbulent pulsation of scale λ will be governed by an equation of the type (3.5)

$$\Delta v \approx v_\lambda (1 - e^{-t/t_0}) . \tag{6.1}$$

Hence it is clear that small-scale pulsations with period $T_\lambda < t_0$ will cause practically no motion of the drop. The disordered motion will be mainly determined by large-scale turbulent pulsations with period $T_\lambda \geqslant t_0$ (or more) and scale

$$\lambda \gtrsim \lambda_* \approx v_{\lambda_*} t_0 \qquad (\lambda_* \approx (v_1 t_0)^{3/2} / d'^{1/2}) . \tag{6.2}$$

If $\lambda_* > d'$, there will be no pulsations in the plasma jet causing appreciable motion of the drops. In this case the effect of turbulence on the motion of the drops can be neglected, and it may be assumed that they move in accordance with the equations of §3 above. When $\lambda_* \ll d'$, there are many pulsations capable of producing disordered motion of the drops. Estimates show that as a rule the first condition is satisfied and the effects of turbulence may be disregarded. The present study does not consider the further disintegration of the fine drops in the turbulent flow, since it has little influence on the results. The diameter d' of the turbulent plasma jet after it leaves the nozzle varies [7] over the range $d < d' < d_0$.

§7. Self-cooling. Formulation of the problem. The plasma jet is the center of complex processes leading to the formation of the target product and a considerable drop in temperature. The detailed description of these processes presents serious difficulties which can not yet be completely overcome. Therefore we shall attempt to estimate the rate of cooling of the plasma jet during the reaction process without resorting to a detailed examination of all the reactions involved. We shall calculate only the total energy absorbed from the hot gas during interaction with the liquid. In order to compute the rate of cooling of the plasma jet we use the equation of heat transfer with negative heat sources (sinks), whose volume density is found by applying the ideas and relations of statistical physics. The reaction energy is assumed to be small.

We shall consider the steady-state problem in the cylindrical coordinate system z, r, φ with origin on the axis of the pipe at a distance $l/2$ from the beginning of the reactor (i.e., the point of introduction of the liquid jets); the zz axis is directed along the axis of the pipe, and l is the unknown linear dimension of the reactor.

In calculating the rate of cooling of the plasma jet we start from the heat transfer equation in the form [4]

$$v_1 \partial S / \partial z = \operatorname{div}(\varkappa \nabla T) - Q + \theta - \theta_j . \tag{7.1}$$

Here S is the entropy of unit mass of gas, κ is its thermal conductivity, θ and θ_j are respectively the energy dissipated per unit time in unit volume and the energy expended in radiation, Q is the energy delivered to the surface of the liquid drops by molecular impact (per unit time per unit volume of gas); it is assumed that Q also includes the energy needed to heat the vapor formed from the liquid to the temperature of the gas-vapor mixture.

For the case in question, the solution of (7.1) written in general form with specific initial and boundary conditions involves serious mathematical difficulties. The approximate solution given below is based on the following simplifying assumptions.

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*Note that in (5.1), which gives the law of variation of the corresponding quantities χ_1, ν_1, and D_1 with variation of R, the denominator may, in fact, contain a large numerical multiplier [4]. To write (5.1) more exactly it is necessary to substitute R/R_* for R [4].

First, in writing the heat transfer equation we confine ourselves to the incompressible-fluid approximation [4]. Second, we consider the steady-state problem in a fixed coordinate system, assuming that the distribution of averaged (with respect to the turbulent pulsations) temperature and concentration established in the reactor depends only on the coordinates. Then, assuming that the averaged-temperature distribution has cylindrical symmetry and neglecting the dependence of the thermal conductivity κ on the coordinates, we rewrite (7.1) in the form

$$c_p\rho_1 v_1 \frac{\partial T}{\partial z} = \varkappa\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial z} + \frac{\partial^2 T}{\partial z^2}\right) - \\ - Q(z, r) + \theta(z, r) - \theta_j(z, r) \ . \tag{7.2}$$

Here c_p is the heat capacity of unit mass of gas.

§8. Estimation of the relative magnitude of the terms in the heat transfer equations. The quantity on the left in Eq. (7.2) and the term in parentheses on the right can be estimated using the relations

$$c_p\rho_1 v_1 \frac{\partial T}{\partial z} \approx c_p\rho_1 \frac{T_{01} - T_f}{l / v_1} > c_p\rho_1 \frac{T_{01} - T_f}{\tau(T_{01})}, \\ \varkappa \frac{\partial^2 T}{\partial z^2} \approx c_p\rho_1 \frac{T_{01} - T_f}{l^2 / \chi_1} \ , \tag{8.1}$$

$$\varkappa \frac{\partial^2 T}{\partial r^2} \approx \frac{\varkappa}{r}\frac{\partial T}{\partial r} \approx c_p\rho_1 \frac{T_1 - T_4}{d_0^2 / 4\chi_1} \qquad \left(\chi_1 = \frac{\varkappa}{c_p\rho_1}\right), \tag{8.2}$$

$$\tau(T) = \tau_0 e^{E/kT} \ .$$

Here T_f is the final temperature of the gas on leaving the reactor, T_4 is the temperature of the gas at the pipe wall, χ_1 is the thermal diffusivity of the gas, $\tau(T)$ is the relaxation time with respect to decomposition of the target product at temperature T.

From the inequalities

$$v_1 l \gg \chi_1 \quad \text{or} \quad l / v_1 \ll l^2 / \chi_1, \qquad d_0^2 / 4\chi_1 \gg l / v_1, \tag{8.3}$$

using (8.1) and (8.2), we get the relations

$$\varkappa \frac{\partial^2 T}{\partial z^2} \ll c_p\rho_1 v_1 \frac{\partial T}{\partial z}, \qquad \varkappa \frac{\partial^2 T}{\partial r^2} \approx \frac{\varkappa}{r}\frac{\partial T}{\partial r} \ll c_p\rho_1 v_1 \frac{\partial T}{qz} \ , \tag{8.4}$$

which enable us to discard the terms in parentheses in the right side of (7.2). We now estimate the quantity $\theta(r)$ which is of the same order as [4]

$$\theta \approx \rho_1 \frac{v_1^3}{d'} + \rho_1 \nu \left(\frac{\partial v}{\partial r}\right)^2 \approx \rho_1 \frac{v_1^3}{d'} + \frac{4\rho_1 \nu v_1^2}{d'^2} \ . \tag{8.5}$$

Since $v_1 d' \gg 4\nu$, we can immediately discard the second term of (8.5). Comparison of the first term in (8.5) with (8.1) leads to the conclusion that for our case $\theta \ll c_p \rho v_1 \partial T/\partial z$, and hence the term $\theta(z,r)$ in (7.2) can be discarded; thus (7.2) may now be rewritten in the simplified form

$$c_p\rho_1 v_1 \frac{\partial T}{\partial z} = - Q(z) - \theta_j(z) \ , \tag{8.6}$$

assuming that the functions Q(z) and $\theta_j(z)$ depend only on the coordinate.

In view of the fact that the negative heat sources that provide for cooling of the plasma jet act on a segment of the z axis equal to l, the function Q(z) satisfies the conditions

$$Q(z) = \begin{cases} 0 & \text{at} \quad z < -{}^1\!/_2 l, \\ Q_0(z) & \text{at} \quad -{}^1\!/_2 l \leqslant z \leqslant {}^1\!/_2 l, \\ 0 & \text{at} \quad z > {}^1\!/_2 l. \end{cases} \tag{8.7}$$

Conditions (8.7) will be automatically satisfied if we represent Q in the form

$$Q(z) = Q_0(z)\,\Delta(z / l), \tag{8.8}$$

where $\Delta(z/l)$ is the discontinuous Dirichlet coefficient

$$\Delta(z / l) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\sin({}^1\!/_2 l\Omega)}{\Omega} e^{i\Omega z}\, d\Omega = \begin{cases} 1 \text{ for } -{}^1\!/_2 l \leqslant z \leqslant {}^1\!/_2 l \\ 0 \text{ otherwise.} \end{cases}$$

The quantities T, c_p, ρ and μ satisfy the conditions

$$T(-{}^1\!/_2 l) = T_{01}, \quad c_p(-{}^1\!/_2 l) = c_{01}, \\ \rho(-{}^1\!/_2 l) = \rho_{01}, \quad \mu(-{}^1\!/_2 l) = \mu_{01} \ . \tag{8.9}$$

where all the quantities with subscript "01" relate to the gas at the beginning of the reactor. The conditions for the function $\theta_j(z)$ can be written down in the same way.

§9. Estimation of the volume density of the negative heat sources (sinks) in the reactor responsible for rapid cooling of the plasma jet. We shall estimate the energy delivered in unit time to the surface of the liquid drops by collision with molecules from unit volume of gas, assuming that close to the drops the velocity distribution of the gas molecules is Maxwellian.

If the gas consists of molecules (of mass m) of one type, then the number of collisions per unit surface and unit time and the kinetic energy of the impacting molecules will be, respectively, [8]

$$f = \frac{p}{\sqrt{2\pi k T m}}, \qquad \varepsilon_0 = p\left(\frac{kT}{\pi m}\right)^{1/2}. \tag{9.1}$$

If the gas consists of molecules of different types, with masses m_i, equations (9.1) remain valid, if the quantities f, p, ε_0, m, f_1, ε_{0i} are determined from the relations

$$f = \sum_i f_i, \quad p = \sum_i p_i, \quad \varepsilon_0 = \sum_i \varepsilon_{0i}, \quad \frac{1}{\sqrt{m}} = \frac{1}{p}\sum \frac{p_i}{\sqrt{m_i}}, \\ f_i = \frac{p_i}{\sqrt{2\pi k T m_i}}, \quad \varepsilon_{0i} = p_i \frac{\sqrt{kT}}{\sqrt{\pi m_i}} \ , \tag{9.2}$$

where the summation is taken over all the components of the gas mixture.

It is known that, generally speaking, not all the energy of the gas molecules colliding with the surface of the drops is transmitted to the surface of the liquid [3, 9].

We shall denote by ω the dimensionless coefficient of energy transfer given by $\omega = \varepsilon/\varepsilon_0$, where ε is the energy transmitted by the gas molecules in unit time to unit surface of liquid;* we isolate in the reactor the cylindrical volume element of gas $dV = \pi d'^2 dz/4$ and calculate the energy $dE(z)$ transmitted to the liquid in unit time by gas molecules colliding with the surface $dS = S_0 dV$ of the drops in this volume; the value of S_0 is obtained from (4.2).

The energy transmitted in unit time to the surface of the liquid by the impact of gas molecules $dE(z) = \varepsilon dS$. Then, assuming that the energy $dE(z)$ is imparted to the surface of the liquid uniformly from the entire volume element of gas dV, we obtain an equation for the energy absorbed at the surface of the drops per cm^2 of gas per second:

$$Q'(z) \approx \frac{dE(z)}{dV} \approx \eta\omega \frac{n\delta^2 v_2 v_1 \rho_1 p}{\alpha d'^2} \left(\frac{kT}{m}\right)^{1/2}. \tag{9.3}$$

In calculating the energy absorbed by the drops from the gas it is necessary to keep in mind the energy

$$Q''(z) = \frac{d}{dV}\left(\frac{dm_2}{dt}\right) \int_{T_{03}}^{T_1} c_2(T)\, dT \tag{9.4}$$

expended on heating the vapor formed as a result of evaporation of the drops from the temperature T_{03} to the temperature of the gas-vapor mixture; here the quantity

$$\frac{d}{dV}\left(\frac{dm_2}{dt}\right) \approx \frac{Q'(z)}{\lambda} \tag{9.5}$$

represents the mass of evaporating liquid per unit time and per unit volume; λ is the specific heat of vaporization; and $c_2(T)$ is the heat capacity of unit mass of vapor. We consider that $T_{03} \ll T_1$, that the interval $\Delta T = T_1 - T_{03} \approx T_1$ is quite large, and that at high temperatures $C_2(T)$ is also large. The result is that in a number of cases $Q'(z)$ and $Q''(z)$ are commensurable. Therefore

$$Q(z) = Q'(z) + Q''(z) = Q'(z)\left[1 + \frac{1}{\lambda}\int_{T_3}^{T_1} c_2(T)\, dT\right]. \tag{9.6}$$

Formally this may be taken into account by introducing the multiplier

$$\omega_0 = \omega\left[1 + \frac{1}{\lambda}\int_{T_3}^{T_1} c_2(T)\, dT\right] > \omega. \tag{9.7}$$

We now consider the energy transmitted by the gas to the drops of liquid in the form of radiation, assuming that the drops constitute a black body. The energy received in unit time by the drops occupying the volume element dV is $dW_j = JdS$, where J is the energy radiated by the gas per second per cm^2; this is equal to

$$J_1 \approx \frac{\Lambda_1}{r}\sigma T_1^4, \qquad J_2 = \frac{r}{\Lambda_2}\sigma T_1^4 \tag{9.8}$$

for optically thick ($r \gg \Lambda_1$) and optically thin ($r \ll \Lambda_2$) bodies, respectively, [10].

Here Λ_1 and Λ_2 are the mean free paths of the radiation in the gas, and r its linear dimensions. The energy loss per second from unit volume of gas by transfer to the drops of liquid is equal to

$$\theta_{j1} = \frac{dW_{j1}}{dV} = j_1 S_0, \qquad \theta_{j2} = \frac{dW_{j2}}{dV} = j_2 S_0 \tag{9.9}$$

for $r \gg \Lambda_1$ and $r \ll \Lambda_2$, respectively.

The condition $\theta_j(z) < Q(z)$, for which the energy losses due to radiation are smaller than the losses due to the impact of gas molecules against the drop surface, may be written in the form

$$\begin{aligned} T^{3.5} &< \frac{\omega_0 r p}{\Lambda_1 \sigma}\left(\frac{k}{\pi m}\right)^{1/2} \quad (r \gg \Lambda_1), \\ T^{3.5} &< \frac{\omega_0 \Lambda_2 p}{r\sigma}\left(\frac{k}{\pi m}\right)^{1/2} \quad (r \ll \Lambda_2). \end{aligned} \tag{9.10}$$

§10. Estimation of the rate of cooling of the plasma jet. From Eqs. (8.6), (9.3), (9.6), and (9.7), provided that radiation can be neglected, it follows that there exists in the reactor along the zz axis a stationary temperature gradient

$$\frac{\partial T}{\partial z} \approx \eta\omega_0 \frac{n\delta^2 v_2 P}{c_p \alpha d'^2}\left(\frac{kT}{m}\right)^{1/2} \Delta\left(\frac{z}{l}\right). \tag{10.1}$$

The total change of temperature on the length l is

$$\Delta T_l = \int_{-1/2 l}^{1/2 l} \frac{\partial T}{\partial z} dz \approx \left(\frac{\partial T}{\partial z}\right)^* l, \tag{10.2}$$

where $(\partial T/\partial z)^*$ is determined from the mean value theorem. Equations (10.1) and (10.2) link the cooling rate and the total temperature change in the reactor with the quantities characterizing the gas (p, T, m, c_p), the liquid (α, λ), its vapor [$c_2(T)$], the operating conditions (v_{01}, v_2), the gas-liquid interaction (ω, η), and the design of the apparatus (δ, d, n, d_0).

The estimates given in (10.1) and (10.2) show that the self-cooling mechanism considered above will operate to cool the plasma jet at a rate fast enough to ensure preservation of the target products.

It should be stressed that in examining this mechanism we have not taken into account the heat effect of the chemical reactions in the gas phase. This approximation is valid for processes in which the heat effect of the reaction is small compared with the quantities considered. In particular, this will be the case when the concentration of the reactants in the gas is relatively low.

In a number of cases when the heat effect of the reaction is large, at a certain stage of the reaction self-cooling can be ensured at the expense of the heat absorbed during the reaction. But this case requires special investigation.

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*Note that the accommodation coefficient β [3, 9] is related to ω as follows

$$\frac{1}{\omega} = \frac{1}{\beta}\left(1 - \frac{\varepsilon_k}{\varepsilon_r}\right).$$

Here ε_k is the mean energy of thermal motion of the molecules of the liquid surface, ε_r is the mean kinetic energy of the gas molecules.

§11. Estimation of effective reactor dimensions and rate of evaporation of the drops. By the term "effective reactor dimensions" we understand the part of the plasma jet or pipe of length l within which more or less all the chemical reactions of any importance are completed, while the temperature of the gas changes from the value T_{01} to a certain value T_f (for example, that below which decomposition of the target product ceases). This definition shows that l depends on the nature of the process, its end purpose and the conditions under which it proceeds. When the entire segment l is characterized by a monotonic decrease in temperature due to cooling (and hence the function $dT/dz < 0$ does not change sign), the value of l is given by (10.2), where we set $\Delta T_l = T_{01} - T_f$.

We will now show under what conditions we are justified in making the above assumption that the drops of liquid are not able to evaporate completely in the reactor.

The mass of liquid supplied to the reactor, calculated per unit time and per unit volume, may be estimated from the relation

$$\frac{d}{dV}\frac{dM}{dt} \approx \frac{\rho_2}{V_0}\frac{\pi\delta^2}{4} v_2 n \qquad \left(V_0 \approx \frac{\pi d_0^2}{4} l\right). \tag{11.1}$$

Here V_0 is the volume of the reactor.

The rate of evaporation is given by (9.5); therefore the fraction of liquid evaporated in the reactor is

$$\gamma \approx \eta\omega \frac{v_2\rho_1 d_0^2 l p}{\alpha\rho_2 d'^2\lambda}\left(\frac{kT}{m}\right)^{1/2}. \tag{11.2}$$

The estimates show that usually $\gamma < 1$; this also justifies the assumption made above. Setting $\gamma < 1$ in (11.2), we can establish the conditions for the satisfaction of this inequality. We can also estimate the time of evaporation of a drop τ_1. In view of the fact that liquids of the water type are poor heat conductors, the drops are not heated through, and hence evaporation proceeds mainly from the surface. Then

$$\tau_1 \approx \int_0^{L_0} \frac{d\varepsilon_1}{(d\varepsilon/dt)} = \frac{\lambda\rho_2 L_1}{\omega\varepsilon_0}. \tag{11.3}$$

Here $d\mathcal{E}_1 = \lambda\rho_2 4\pi R^2 dR$ is the energy required to evaporate the surface layer of the drop, R is the radius of the drop, $d\mathcal{E}/dt = \omega\mathcal{E}_0 4\pi R^2$ is the energy supplied to the drop per second by molecular impact. Estimates show that the time τ_1 is usually greater than the time taken by the drop to pass through the reactor, which may be estimated from (3.3)–(3.5) and (10.2). This conclusion is in accord with the condition $\gamma < 1$, which allows us to assume that the drops are not completely evaporated in the reactor.

The above discussion shows that one of the characteristic features of plasmochemical processes is the complex interweaving of the various mechanical, physical and chemical effects. Therefore the analysis of such processes demands the combined application of the ideas and methods of various branches of mechanics, physics and chemistry.

It is a specific feature of these processes that the chemical reactions and self-cooling exert a considerable effect on the hydrodynamic parameters of the system: density, flowrate, kinematic viscosity, etc. This means, in particular, that there is a change in the Reynolds number of the plasma jet in the reactor. Then the gas flow in the reactor is characterized by nonuniform turbulence.

Thus, plasmochemical reactions are nonisothermal reactions proceeding in a flow whose Reynolds number is a function of the coordinate.

In view of the fact that it is still virtually impossible to construct a rigorous theory of plasmochemical processes, we may expect significant results from application of the methods of dimensional analysis and similarity theory not only to the mechanical and physical phenomena but also to the chemical processes (see, for example, [11]).

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