ENERGETICS OF PLASMA-CHEMICAL SYSTEMS IN SELECTIVE TRANSFER PROCESSES

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A diffusion model is proposed for the theoretical investigation of how diffusive heat and mass transfer affects the energetics of the plasma-chemical process in highly spatially inhomogeneous discharge systems.

The type of plasma-chemical systems customarily used most extensively to carry out endoergic chemical reactions is that of discharges with a thermal plasma [1]. Products are obtained in such reactions according to a comparatively simple scheme: thermal heating–nonadiabatic cooling (quenching). In the analysis of such systems the minimum energy expenditure for obtaining a unit product is assumed not to depend on the heat and mass exchange and can be determined by the conventional method of thermodynamic calculation [2]. As was shown in [3], however, when sufficiently large external forces act on a system the flux of product from the reaction zone can increase relative to the flux of thermal and chemical energy (the transfer of energy and material becomes a selective process), which means a reduction of the minimum energy expenditure. Such a situation, as will be shown below, is also characteristic of highly spatially inhomogeneous systems in which the removal of heat and products from the reaction zone is determined by molecular diffusion in this paper we study the effect of the selectivity of the transfer process on the energy efficiency of chemical processes in highly spatially inhomogeneous systems.

Our analysis of how the selective nature of the heat and mass transfer, owing to the difference in the diffusion coefficients, affects the energetics of the chemical reactions will be conducted within the framework of the following model: the temperature distribution in the discharge region is uniform; the starting materials are delivered into the reaction zone and products are removed by diffusion; the temperature and concentration of the products at the periphery are kept constant at T^r and 0, respectively. The energy expenditure for obtaining the product within this model is determined by the ratio of the total enthalpy flux q out of the reaction zone to the product flux j_n.

$$A \equiv \frac{q}{j_n} = \frac{-\lambda \nabla T + \sum_{i=1}^{N} I_i j_i}{j_n}, \tag{1}$$

here λ is the thermal conductivity coefficient of the gas mixture, $j_i = m_i n_i V_i$ is the mass flux of the i-th component, (m_i, n_i, and V_i, respectively, are the molecular mass, concentration, and rate of diffusion of the i-th component), and I_i is the enthalpy (with allowance for the enthalpy of formation) per unit mass of the i-th component. As is seen from Eq. (1), energy is removed from the reaction zone by means of ordinary thermal conductivity and diffusive transfer of chemical and thermal energy by each component.

The transfer equations take on the comparatively simple form [3]

$$q = -\rho D \nabla I, \quad j_i = -\rho D \nabla Y_i \tag{2}$$

upon satisfaction of the following conditions:* 1) that the diffusion coefficients for all the components be equal, $D_{ij} = D$; 2) that thermal diffusion does not occur, $D_i^T = 0$; and 3)

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*We note that in the case of turbulent exchange these conditions are satisfied antomatically.

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that the Lewis number Le = $\lambda/\rho c_p D$ be equal to unity (ρ is the density $c_p = \sum_{i=1}^{N} Y_i \frac{\partial I_i}{\partial T}$ is the heat capacity of the mixture and $Y_i = \rho_i/\rho$ is the mass fraction of the i-th component). The minimum possible energy expenditure is determined in this case by the equation [3]

$$A_0 = \frac{I(T^l) - I(T^r)}{Y_n^l}, \tag{3}$$

where $I = \sum_{i=1}^{N} I_i Y_i$ is the total enthalpy per unit mass of mixture, T^{ℓ} and T^{r} are the temperatures in the heating region and at the periphery and Y_n^{ℓ} is mass fraction of product in the reaction zone, which is determined only by the heating temperature T^{ℓ} and the pressure in the system. We note that the minimum energy expenditure does not depend on the transfer coefficients [because of the similarity of the fluxes of the total enthalpy and products (2)] and is equal to the value calculated by the thermodynamic method [2].

Since in real discharge systems the conditions given above are not satisfied, in general, the resulting situation is one in which the composition in the reaction zone and the limiting energy expenditure begins to depend explicitly on the relations between the transfer coefficients. This dependence is due mainly to the following factors.

1. The thermal diffusivity coefficient $\kappa \equiv /(\lambda c_p$ of the mixture differs from the binary diffusion coefficients of the reagents (which determine the transfer of the material and as a rule have a value higher than κ) creates conditions under which the product flux from the reaction zone can substantially exceed the heat flux.

II. Due to the different binary diffusion coefficients of the reagents the reaction zone is slowly enriched with diffusing components; this accelerates the entire mass transfer but has virtually no effect on the heat flux.

III. The difference in the binary diffusion coefficients can also cause a change in the relations between the reagent fluxes and, hence, a change in the amount of chemical energy removed from the reaction zone per molecule of product.

As a result of these effects, both the thermal energy and the chemical energy per unit of procout carried out depend essentially on the heat and mass transfer coefficients.

Let us now analyze the importance of these effects in greater detail. First let us determine the dependence of the minimimum energy expenditure on the relation between the thermal diffusivity coefficient and the binary diffusion coefficients. For this purpose we consider a chemical process in which all reagents have identical binary diffusion coefficients $D_{ij} = D$, $1 \neq j$ and, generally speaking, different self-diffusion coefficients (which, in the general case, means $\kappa \neq D$). When this is taken into account, the transfer equations in the one-dimensional stationary case become

$$j_i = -\rho D \frac{\partial}{\partial x} Y_i, \tag{4}$$

$$q = -\lambda \frac{\partial}{\partial x} T - \rho D \sum_{i=1}^{N} I_i \frac{\partial}{\partial x} Y_i. \tag{5}$$

It is convenient to rewrite the last equation as

$$q = -\rho D \frac{\partial}{\partial x} I - \rho D c_p \left(1 - \frac{\varkappa}{D}\right)\left(-\frac{\partial}{\partial x} T\right). \tag{6}$$

The second term on the right side of Eq. (6) is a correction to the total enthalpy flux for the difference between the thermal diffusivity coefficient κ and the mass transfer coefficient D. Within the framework of the diffusion model under consideration the equations of the conservation of energy and continuity of the fluxes of the chemical components take on the form

$$0 = \frac{\partial}{\partial x}\left[\rho D \frac{\partial}{\partial x} I - \rho D c_p \left(1 - \frac{\varkappa}{D}\right) \frac{\partial}{\partial x} T\right], \tag{7}$$

$$0 = \frac{\partial}{\partial x}\left[\rho D \frac{\partial}{\partial x} Y_i\right] + m_i \omega_i, \tag{8}$$

where ω_i is the chemical reaction rate, calculated for the i-th component. Since, as is seen from (4), all the products are transported in the same way and the concentration of reagents in the reaction zone is constrained by the condition of chemical equilibrium, the composition in the discharge zone does not depend on the transfer coefficient. When this is taken into account, the boundary conditions for the total enthalpy and the reagent concentrations become $I|_{x=l}=I(T^l)$, $I|_{x=r}=I(T^r)$, $Y_i|_{x=l}=Y_i(T^l)$, $Y_n|_{x=r}=0$. In order to calculate the maximum flux of product from the reaction zone the chemical-reaction term should be set equal to zero in the region of high temperature gradients and reagent concentrations. In this case integration of Eqs. (7) and (8) over x gives

$$j_n \int_l^r \frac{dx}{\rho D} = Y_n^l, \tag{9}$$

$$q \int_l^r \frac{dx}{\rho D} = I(T^l) - I(T^r) - \int_{T^r}^{T^l} \left(1 - \frac{\varkappa}{D}\right) c_p dT. \tag{10}$$

The ratio of these expressions determines the minimum possible energy expenditure,

$$A = A_0 \left[1 - \frac{\int_{T^r}^{T^l} c_p \left(1 - \frac{\varkappa}{D}\right) dT}{I(T^l) - I(T^r)}\right]. \tag{11}$$

Comparison of Eqs. (11) and (13) shows that the minimum energy expenditure for a given chemical process, obtained by the modynamic calculation, differs from the limiting energy expenditure taking into account the selectivity of the transfer processes by a corrective term, which is proportional to the relative deviation of the thermal diffusivity coefficient from the mass transfer coefficient. As follows from the calculation above, this is because in the case $\varkappa < D$ ($\varkappa > D$) more (less) heat per molecule of product will be removed than in the reaction zone. Equation (11) can be put into analytical form (by substituting the general expression for $\varkappa$ [4] and then integrating), but is rather complicated and cumbersome in the general case. The simplest case is obtained for chemical processes in which the relation $\frac{X_1}{D_{11}} \gg \frac{1-X_1}{D}$ ($X_i = n_i/n$ is the molar component of the i-th component) is satisfied in the reaction zone for one of the components (we label it with i = 1). In this case the thermal conductivity of the mixture is in fact determined by the first component and Eq. (11) takes on the form

$$A = A_0 \left[1 - \frac{D - D_{11}}{D} \frac{\int_{T^r}^{T^l} c_p dT}{I(T^l) - I(T^r)}\right]. \tag{12}$$

Thus, as is seen from Eqs. (11) and (12), the difference between the thermal diffusivity coefficient and the binary diffusion coefficients causes a change in the relation between the product flux and the heat flux and, hence, reduces the energy expenditure involved in useless heating of the reagents by a factor of $D/\varkappa$.

These expressions permit, e.g., a fairly accurate calculation of the effect that the selectivity of the transfer processes have on the energetics of the chemical process $M_2 \rightleftarrows 2M$. The transfer of material here is determined by one coefficient $D_{M_2,M}$, while the heat transfer is determined mainly by the thermal conductivity M_2 ($\varkappa \approx D_{M_2,M_2}$). The minimum energy expenditure in this case will be determined by

$$A = A_0 \left[1 - \frac{D_{M_2,M} - D_{M_2,M_2}}{D_{M_2,M}} \frac{\int_{T^r}^{T^l} c_p dT}{I(T^l) - I(T^r)}\right]. \tag{13}$$

Calculation from Eq. (13) for the process $O_2 \rightleftarrows 2O$, $N_2 \rightleftarrows 2N$, $H_2 \rightleftarrows 2H$ showed that the values of the minimum energy expenditure in the case of diffusive transfer processes decrease from 6.6, 12.6, and 6.2 eV to 5.8, 12.35, and 5.75 eV, respectively (p = 0.1 torr).

Let us now determine the dependence of the limiting energy expenditure when the binary diffusion coefficients of the reagents differ. It is convenient to distinguish two cases here. In the first case, in order to eliminate the effect due to a change in the relations between the reagent fluxes, we consider a chemical process in which only one dissociation reaction $A^0 \rightleftarrows \sum_{i=1}^{N} \nu_i A_i$ occurs, forming a useful product A_i (as can be easily shown, the fluxes of the resulting substances A_i are related by the stoichiometric ratio and, therefore, the amount of chemical energy removed per molecule of A_i does not depend on the transfer coefficients). We assume that, generally speaking, the reagents have different binary diffusion coefficients. The transfer equations in the one-dimensional stationary case with only small degrees of decomposition of the initial substance A^0 take on the form

$$j_i = -\rho D_{i0} \frac{\partial}{\partial x} Y_i, \quad i = \overline{1, N}, \quad j_0 = -\sum_{i=1}^{N} j_i, \tag{14}$$

$$q = -\lambda \frac{\partial}{\partial x} T + \sum_{\alpha=0}^{N} I_\alpha j_\alpha. \tag{15}$$

Since the fluxes of products A_i and A_h are related by the stoichiometric ratio

$$\frac{j_i}{\nu_i m_i} = \frac{j_k}{\nu_k m_k}, \quad i, k = \overline{1, N}, \tag{16}$$

inclusion of (14) gives

$$\frac{D_{i0}}{m_i \nu_i} \frac{\partial}{\partial x} Y_i = \frac{D_{k0}}{m_k \nu_k} \frac{\partial}{\partial x} Y_k. \tag{17}$$

Integrating the last equation over x from r to x, we find the relation between the molar concentrations of the products

$$D_{i0} \frac{X_i}{\nu_i} = D_{k0} \frac{X_k}{\nu_k}. \tag{18}$$

Equation (18) was obtained without any assumptions as to the relation between the diffusion rate and the chemical reaction rate and is thus valid for any point of the system (including the reaction zone) for any degree of spatial inhomogeneity (the sole condition here is that the transfer processes be diffusive). Since the concentrations of the products and the initial substance in the reaction zone are related by the equation of chemical equilibrium

$$K(T^l) = \frac{\prod_{i=1}^{N} (X_i^l)^{\nu_i}}{1 - \sum_{i=1}^{N} X_i^l} n^{f-1}, \quad f = \sum_{i=1}^{N} \nu_i, \tag{19}$$

we can use Eq. (18) to find the changed composition

$$X_i^l = X_i^{(0)} \prod_{k=1}^{N} \left(\frac{D_{k0}}{D_{i0}} \right)^{\nu_k / f}, \tag{20}$$

where $X_i^{(0)}$ is the thermodynamic concentration of product A_i at temperature T^l. From (20) we see that the ratio of X_i^l and $X_i^{(0)}$ does not depend on the temperature in the reaction zone and is a function of only the relations of the binary diffusion coefficients. In particular, $X_i^l = X_i^{(0)}$ at $D_{10} = D$. We can easily ascertain that the concentration of the rapidly diffusing component decreases and that of the slowly diffusing component increases. Since during the diffusion the product flux can only decrease (because of the endoergic nature of the chemical process), in a calculation of the maximum product flux and the minimum energy expenditure the chemical-reaction term must be set equal to zero in the region of large concentration and temperature gradients. Then, after integrating (14) and (15) and taking (20) and $\kappa \approx D_{00}$ into account, we can easily obtain an expression for the limiting energy expenditure

$$A = A_0 \left[1 - \frac{\tilde{D} - D_{00}}{\tilde{D}} \frac{\int_{T^r}^{T^l} c_p dT}{I(T^l) - I(T^r)} \right], \tag{21}$$

where $\tilde{D} = \prod_{i=1}^{N} (D_{i0})^{\nu_i / f}$.

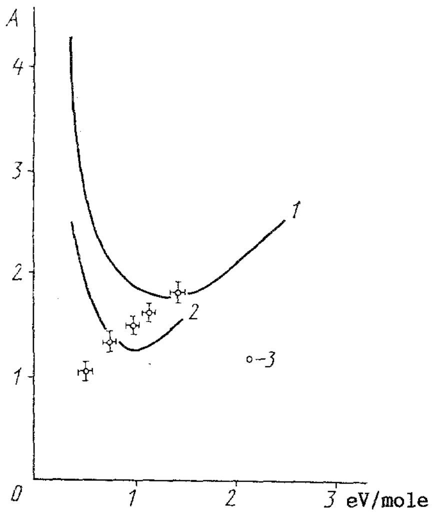

Fig. 1. Limiting energy expenditure A as a function of the specific energy input ε. Calculation 1) ideal quenching [7]; 2) with allowance for the selectivity of the transfer processes, owing to the difference in the diffusion coefficients. Experiment 3) in the presence of a centrifugal field [7]

The form of Eq. (21) is analogous to that of (11)-(13). The only difference, but a very important one, is that we have an effective coefficient D here instead of a single binary diffusion coefficient. This coefficient is obtained by solving the self-consistent problem and makes allowance for both the rate at which each product is removed and the change in the reaction zone as a result of the difference in the mass transfer coefficients. Since $D_{i0} > D_{00}$ as a rule, a situation arises in which the product flux from the reaction zone exceeds the heat flux and, consequently, the energy expenditure for useless heating of the gas mixture is reduced by a factor of $\tilde{D}/D_{00}$.

Equation (21) makes it possible to calculate the minimum energy expenditure fairly accurately with allowance for the selectivity of the transfer processes during thermal decomposition of hydrogen sulfide, H_2S. Since in this case the concentration of radical is low over a wide temperature range [5], we can consider the gas mixture as a three-component mixture (H_2S, H_2, S_2) with the following relations between the diffusion coefficients $D_{S_2,H_2S} \simeq D_{H_2S,H_2S}$, $D_{H_2,H_2S} \simeq D_{H_2,S_2} \simeq 3{,}5 D_{H_2S,H_2S}$. The heat flux is then determined mainly by the thermal conductivity of H_2S and S_2, while the relatively large H_2 transfer coefficient results in the acceleration of the entire mass transfer. Calculation of Eq. (21) for the given chemical process (the energy input is considered below) is shown in Fig. 1, from which we see that the effect described here reduces the minimum possible energy expenditure from 1.8 to 1.3 eV.

The effects considered above allow the minimum energy expenditure to be decreased because of a relative reduction of the heat flux in comparison with the product flux. When the binary diffusion coefficients differ and several reactions occur in the system, however, there can be an effect due to the change in the relations between reagent fluxes, as a result of which the amount of chemical energy removed per product molecule also changes. For simplicity of calculation of this effect we consider a chemical process in which two independent dissociation reactions

$$A^0 \rightleftarrows \sum_{i=1}^{N} \nu_i A_i, \quad B^0 \rightleftarrows \sum_{\alpha=1}^{M} \mu_\alpha B_\alpha$$

occur, useful product A_1 being formed in the first reaction. Suppose that the self-diffusion coefficients of the initial substances and their binary diffusion coefficient are equal to each other ($D_{A^0,A^0} = D_{A^0,B^0} = D_{B^0,B^0}$) and that the binary diffusion coefficients of the products of the first and second reactions satisfy the conditions $D_{A_i,A^0} = D_{A_i,B^0} = D_{i0}$, $D_{B_\alpha,A^0} = D_{B_\alpha,B^0} = D_{\alpha 0}$. Then for low degrees of decomposition the transfer equations become

$$j_i = -\rho D_{i0} \frac{\partial}{\partial x} Y_i,\quad i = \overline{1, N},\quad j_{A^0} = -\sum_{i=1}^{N} j_i, \tag{22}$$

$$j_\alpha = -\rho D_{\alpha 0} \frac{\partial}{\partial x} Y_\alpha,\quad \alpha = \overline{1, M},\quad j_{B^0} = -\sum_{\alpha=1}^{M} j_\alpha, \tag{23}$$

$$q = -\rho D_{00} c_p \frac{\partial}{\partial x} T + j_{A_1} \Delta I_1 + j_{B_1} \Delta I_2, \tag{24}$$

where ΔI_1 and ΔI_2 are the enthalpies of the first and second chemical reactions per unit mass of products A_1 and B_1, respectively. Carrying out calculations analogous to (14)-(19), separately for each reaction, we find the composition in the reaction zone,

$$X_i^l = X_i^{(0)} \prod_{k=1}^{N} \left(\frac{D_{k0}}{D_{i0}} \right)^{\nu_k / f_1},\quad f_1 = \sum_{i=1}^{N} \nu_i, \tag{25}$$

$$X_\alpha^l = X_\alpha^{(0)} \prod_{\beta=1}^{M} \left(\frac{D_{\beta 0}}{D_{\alpha 0}} \right)^{\mu_\beta / f_2},\quad f_2 = \sum_{\alpha=1}^{M} \mu_\alpha, \tag{26}$$

where $X_i^{(0)}$ and $X_\alpha^{(0)}$ are the thermodynamic concentrations calculated for temperature T^l. The energy efficiency of the given chemical process when there are large spatial inhomogeneities is calculated by integrating Eqs. (22)-(24) (assuming that $\omega_i = \omega_\alpha = 0$) with allowance for the boundary conditions $Y_\alpha^r = Y_i^r = 0$ [Eqs. (25), (26)]:

$$A = A_0 \left[1 - \frac{\tilde{D}_1 - D_{00}}{\tilde{D}_1} \frac{\int_{T^r}^{T^l} c_p dT}{I(T^l) - I(T^r)} - \frac{\tilde{D}_1 - \tilde{D}_2}{\tilde{D}_1} \frac{\Delta I_2 Y_{B_1}^{(0)}}{I(T^l) - I(T^r)} \right]; \tag{27}$$

here $\tilde{D}_1 = \prod_{i=1}^{N} (D_{i0})^{\nu_i / f_1}$ and $\tilde{D}_2 = \prod_{\alpha=1}^{M} (D_{\alpha 0})^{\mu_\alpha / f_2}$. We see that this expression differs from (21) by the presence of an additional correction, which is positive (negative) when $\tilde{D}_2 < \tilde{D}_1$ ($\tilde{D}_2 > \tilde{D}_1$). This correction is for the change in the relations between the products fluxes of the first and second reactions, the removal of which is determined by the effective coefficients $\tilde{D}_1$ and $\tilde{D}_2$. As a result, the amount of chemical energy per molecule of useful product A_1 changes (increases when $\tilde{D}_2 > \tilde{D}_1$ and decreases when $\tilde{D}_2 < \tilde{D}_1$). Even though Eq. (27) was obtained in the approximation of two independent reactions, when there are several reactions (which make the calculations much more complicated) the essence of this correction remains the same, namely, with a difference in the mass transfer coefficients a disproportional change occurs in the reagent fluxes. For example, in the thermal decomposition of carbon dioxide CO_2 the comparatively large transfer coefficient of atomic oxygen O (roughly 6-10 times that of the other reagents) can result in its flux increasing 3-4 times in comparison with the CO flux and the energy expenditure for obtaining CO rises by 1-2 eV.

In the calculations above we determined the minimum energy expenditure of the reaction zone temperature and the relations between the transfer coefficients. Let us now consider the problem of determining the energy input.

In the given diffusion model it would be natural to define the energy input as the ratio of the total enthalpy flux from the reaction zone to the flux of the initial substance diffusing into the discharge region. It is necessary to specify here, however, what is meant by the flux of the initial substance and how to find it. If, as before, this flux is taken to mean the flux determined from the condition that the mean mass velocity be zero (all the mass transfer equations in this paper have been obtained from a system consisting of the (N − 1)-st Stefan-Maxwell equation [4, 6] with the auxiliary condition $\sum_{\alpha=1}^{N} j_\alpha = 0$), then, as can be easily shown, the energy input is equal to the energy expenditure to within a constant factor. This difficulty can nevertheless be obviated with comparative ease by formally dividing the initial substance into two components: 1) the initial substance in the reaction zone and 2) the initial substance at the periphery. The transfer of substance will now be described by the (N + 1)-st diffusion equation. This procedure makes it possible to isolate two fluxes of the initial substance: 1) the flux $j_{\text{init}}^{\text{in}}$ in the reaction zone and 2) the

$j_{\text{init}}^{\text{out}}$ from the discharge region. This method can be used to determine both the energy input $\varepsilon \equiv q/j_{\text{init}}^{\text{in}}$ and the degree of decomposition $\eta \equiv (j_{\text{init}}^{\text{in}} - j_{\text{init}}^{\text{out}})/j_{\text{init}}^{\text{in}}$. Without given all the rather simple calculations here, we immediately write out energy input expressions which complement (3), (11), (21), and (27), respectively:

$$\varepsilon = I(T^l) - I(T^r), \tag{28}$$

$$\varepsilon = I(T^l) - I(T^r) - \int\limits_{T^r}^{T^l} \left(1 - \frac{\varkappa}{D}\right) c_p dT, \tag{29}$$

$$\varepsilon = \frac{I(T^l) - I(T^r) - \left(1 - \dfrac{D_{00}}{\tilde{D}}\right) \int\limits_{T^r}^{T^l} c_p dT}{\dfrac{D_{00}}{\tilde{D}} + \dfrac{X_1^{(0)}}{\nu_1}\left(1 - \Sigma\nu_i \dfrac{D_{00}}{D_{i0}}\right)} \left(1 + \frac{X_1^{(0)}}{\nu_1}(1 - f)\right), \tag{30}$$

$$\begin{aligned}\varepsilon = {} & \left[I(T^l) - I(T^r) - \frac{\tilde{D}_1 - D_{00}}{\tilde{D}_1} \int\limits_{T^r}^{T^l} c_p dT - \frac{\tilde{D}_1 - \tilde{D}_2}{\tilde{D}_1} \Delta I_2 Y_{B_1}^{(0)}\right] \times \\ & \times \left[m_{A^0} X_{A^0}^r + m_{B^0} X_{B^0}^r + \frac{X_{A_1}^{(0)}}{\nu_1}(1 - f_1) + \frac{X_{B_1}^{(0)}}{\mu_1}(1 - f_2)\right] \times \\ & \times \left\{\frac{D_{00}}{\tilde{D}_1}[m_{A^0} X_{A^0}^r + m_{B^0} X_{B^0}^r] + m_{A^0} \frac{X_{A_1}^{(0)}}{\nu_1}\left(1 - \Sigma\nu_i \frac{D_{00}}{D_{i0}}\right) + \right. \\ & + m_{B^0} \frac{\tilde{D}_2}{\tilde{D}_1} \frac{X_{B_1}^{(0)}}{\mu_1}\left(1 - \Sigma\mu_\alpha \frac{D_{00}}{D_{\alpha 0}}\right) + \frac{X_{A_1}^{(0)}}{\nu_1}(m_{A^0} X_{B^0}^r - m_{B^0} X_{B^0}^r) + \\ & \left. + \frac{\tilde{D}_2}{\tilde{D}_1}(m_{B^0} - m_{A^0}) X_{A^0}^r \frac{X_{B_1}^{(0)}}{\mu_1}\right\}^{-1}.\end{aligned} \tag{31}$$

We note that in Eqs. (30) and (31) the values of the energy input, as a rule, are higher than those obtained from the modynamic calculation (28), owing to the higher degree of decomposition of the initial substances. Using Eqs. (29)-(31), we can plot the parametric curves of the energy expenditure versus the energy input (the temperatures in the reaction zone and at the periphery as well as the ratios between the transfer coefficients are the parameters). One such curve, plotted for the thermal decomposition of H_2S is shown in Fig. 1. We point out that even when allowance is made for the selectivity of the transfer processes, owing to the difference in the diffusion coefficients, an explanation still does not present itself for the experimental data (see Fig. 1) obtained in a rapidly rotating plasma-chemical system. This is because when fairly large centrifugal forces act on a system in which the reagents have significantly different molecular masses, mass transfer becomes a drift process, thus creating conditions for an increase in the product flux relative to the heat flux. If, moreover, a condensing product (sulfur S_2 in the case of the decomposition of H_2S) is formed as a result of the reaction, the centrifugal forces can cause the product to be removed primarily in the condensed phase, thus lowering the energy expenditure for the chemical reaction as such.

Let us now analyze the dependence of the minimum energy expenditure when the conditions imposed on the model under consideration are changed (the diffusive nature of the transfer processes, etc.).

2. A nonzero product concentration on the periphery, virtually not changing the heat flux, causes the product flux to decrease and, therefore, the energy expenditure to rise.

3. If there is a nonuniform temperature distribution in the discharge zone, the initial substance will decompose in a certain temperature range. The energy efficiency and the energy input of the decomposition process in this are found in this case, on the whole, by averaging. Solution of this problem becomes complicated and for that reason we confine our discussion here to a qualitative explanation of the effect that the averaging procedure has on the dependence of the energy expenditure on the energy input. First we assume that one part of the initial substance decomposes at temperature $T^{(1)}$ while the other decomposes at

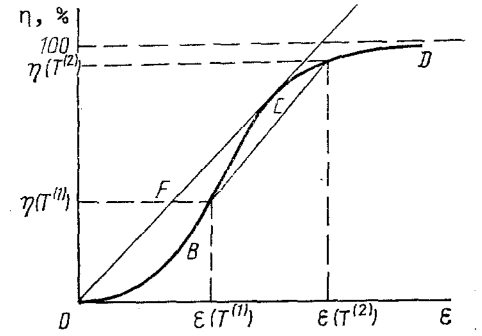

Fig. 2

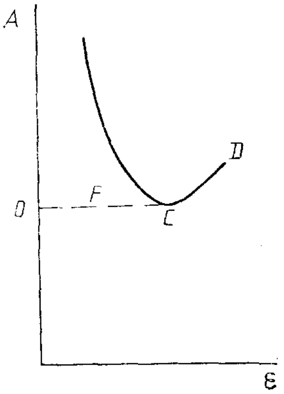

Fig. 3

Fig. 2. OBCD represents the dependence of the energy expenditure on the energy input ε, calculated for the diffusion model.

Fig. 3. FCD represents the dependence of the energy expenditure A on the energy input, calculated for the diffusion model; OFCD is the curve delineating the region of possible values of the energy expenditure A^{av} and the energy input ε^{av}.

$T^{(2)}$ ($T^{(2)} > T^{(1)}$). In this case the average energy input ε^{av} and degree of decomposition η^{av} are determined by

$$\eta^{av} = \eta(T_1^{(1)}) + (1 - \eta(T^{(1)}))\,\eta(T^{(2)}), \tag{32}$$

$$\varepsilon^{av} = \varepsilon(T^{(1)}) + [\varepsilon(T^{(2)}) - \varepsilon(T^{(1)})]\,\frac{\eta^{av}\eta(T^{(1)})}{\eta(T^{(2)})}, \tag{33}$$

where ε(T) and η(T) are the energy input and the degree of conversion, calculated for the model with a uniform distribution of the temperature T in the reaction zone. Graphically, Eqs. (32) and (33) correspond to the situation when (see Fig. 2) point ($\eta^{av}\varepsilon^{av}$) lies on the segment $[(\eta(T^{(1)}), \varepsilon(T^{(1)}));\ (\eta(T^{(2)}), \varepsilon(T^{2}))]$. Taking this into account, we can easily show that curve OFCD now is the curve delineating the region of possible values of η^{av} and ε^{av}. This circumstance causes a considerable change in the dependence of the energy expenditure on the energy input (see Fig. 3). Such discussions can also be carried out in the general case of averaging. The main conclusions stemming from the above are: a) the curve of A^{av} as a function of ε^{av} will also lie above the curve OFCD, lying higher when the range of discharge zone temperatures is wider; b) the minimum energy expenditure is obtained with a uniform temperature distribution in the reaction zone (the minimum energy expenditure corresponds to point C in Figs. 2 and 3). The diffusion model thus does indeed describe the maximum effect of the selectivity of the transfer processes on the energetics of the chemical reactions in a thermal plasma.

In summary, the main conclusion of this study is that the selectivity of the processes of heat and mass transfer, owing to the difference in the diffusion coefficients, results in an explicit dependence of the energy input and minimum energy expenditure on these coefficients. The analytical expressions derived here make it possible to determine this dependence for a fairly broad class of chemical processes.

NOTATION

Here A is the energy expenditure; ε is the energy input; λ is the thermal conductivity coefficient; T is the temperature; I is the enthalpy; D_{ij} are the binary diffusion coefficients; ρ is the gas density; q is the total enthalpy flux; j_i is the flux of the i-th substance; X_i and Y_i are the molar and mass concentrations of the i-th component; C_p is the heat capacity of the gas; and the α is the thermal diffusivity coefficient.

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