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INFLUENCE OF STEFAN FLOW ON HEAT AND MASS TRANSFER AND KINETICS OF CHEMICAL REACTIONS OF A CARBON PARTICLE IN AIR

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With account taken of Stefan flow, an analysis of the interrelated heat and mass transfer of a carbon particle in parallel reactions on its surface is performed.

When parallel reactions ($C+O_2 \to CO_2$ and $2C+O_2 \to 2CO$) proceed on the surface of a carbon particle, a Stefan flow develops which leads to a decrease in the oxidant mass flux and enhances heat removal [1-3]. The available literary sources [1-3] do not give in an explicit form the expressions for heat and mass fluxes, the power of heat releases, and the concentrations of gaseous components allowing for Stefan flow. Here we derive expressions for the interrelated heat and mass fluxes on the particle surface, surface power of heat release, and rates of heterogeneous reactions allowing for Stefan flow. Temperature and concentration profiles are obtained for the components in the gaseous phase. This enables us to perform an analysis of the influence of Stefan flow on the characteristics of heterogeneous combustion of a carbon particle: the induction period, the combustion time and temperature, and the critical conditions of heat and mass transfer (HMT) governing the limits of heterogeneous combustion [4-6].

Analyzing the heterogeneous ignition, combustion, and extinction of the carbon particle shows the need for taking account of two parallel reactions: $C+O_2 \to CO_2$(I) and $2C+O_2 \to 2CO$ (II) [4-6]. Since Bi0 << 1, the temperature gradient over the particle can be ignored. In this case the equation of heat balance for the particle appears as

$$\frac{1}{6} c_1 \rho_1 d \frac{dT_1}{dt} = Q_x - (Q_\lambda + Q_{st}) - Q_r , \quad T_1 (t = 0) = T_{in} . \tag{1}$$

The heat release power as a result of the heterogeneous reactions is

$$Q_x = (k_1 q_1 + k_2 q_2) \rho_{2R} C_{1R} , \tag{2}$$

where

$$k_1 = k_{01} \exp \left(- \frac{E_1}{RT_1} \right) , \quad k_2 = k_{02} \exp \left(- \frac{E_2}{RT_1} \right) .$$

The density of the heat flux from the particle via molecules and via Stefan flow is

$$Q_{\lambda\, st} = Q_\lambda + Q_{st} = - \lambda_2 \left. \frac{\partial T_2}{\partial r} \right|_R + (\rho_2 v)_R \, c_2 T_2 . \tag{3}$$

The density of the heat flux by radiation is determined by the Kirchhoff and Stefan-Boltzmann laws:

$$Q_r = \varepsilon \sigma (T_1^4 - T_w^4) .$$

To find C_{1R}, $(\rho_2 v)_R$, and $Q_{\lambda\, st}$, we need to solve diffusion, continuity, and heat conduction equations for the gaseous phase. Since the coefficients of thermal diffusivity and diffusion for the gaseous components are higher

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than the coefficient of thermal diffusivity for the particle, the times in which stationary concentration and temperature fields are established in the gaseous phase can be considered as being smaller than the time in which a stationary field is established in the particle. This allows us to use for the gas the equations of stationary processes

$$\frac{\partial}{\partial r}\left(r^2\lambda_2\frac{\partial T_2}{\partial r}\right) = \frac{\partial}{\partial r}(c_2T_2\rho_2vr^2),$$

$$\frac{\partial}{\partial r}\left(r^2\rho_2D\frac{\partial C_j}{\partial r}\right) = \frac{\partial}{\partial r}(C_j\rho_2vr^2),$$

$$\frac{\partial}{\partial r}(\rho_2vr^2) = 0. \tag{4}$$

We write the boundary conditions:

$$T_2(r=R) = T_{2R}, \quad \sum_{j=1}^{4} C_{jR} = 1; \; T_2(r=\infty) = T_{2\infty}, \quad \sum_{j=1}^{4} C_{j\infty} = 1. \tag{5}$$

The density of the oxygen flux is

$$j_{1R} = \rho_{2R}C_{1R}(k_1+k_2),$$

of the CO_2 flux:

$$\frac{j_{2R}}{\mu_2} = \frac{k_1\rho_{2R}C_{1R}}{\mu_1}, \tag{6}$$

of the CO flux:

$$\frac{j_{3R}}{2\mu_3} = \frac{k_2\rho_{2R}C_{1R}}{\mu_1},$$

of the nitrogen flux: $j_{4R} = 0$.

The velocity of the Stefan flow is determined by the algebraic sum of the flux densities on the particle surface:

$$(\rho_2v)_R = j_{2R} + j_{3R} - j_{1R} = \frac{\mu_5}{\mu_1}(k_1+2k_2)\rho_{2R}C_{1R}, \tag{7}$$

where μ_5 is the molar weight of the carbon.

It is convenient to represent the solution (4) as

$$\frac{dC_j}{dr} - \frac{(\rho_2v)_R}{\rho_2D}\left(\frac{R}{r}\right)^2 C_j = \frac{(\rho_2v)_R}{\rho_2D}\left(\frac{R}{r}\right)^2 \beta_j,$$

$$\frac{dT_2}{dr} - \frac{(\rho_2v)_R}{\rho_2D}\left(\frac{R}{r}\right)^2 T_2 = \frac{(\rho_2v)_R}{\rho_2D}\left(\frac{R}{r}\right)^2 \beta,$$

$$\rho_2vr^2 = (\rho_2v)_R R^2 = \text{const}.$$

Introducing the new variable

$$\xi = \int_r^\infty \frac{(\rho_2v)_R}{\rho_2D}\frac{R^2}{r^2}\,dr,$$

we obtain

$$\frac{d\,(C_j+\beta_j)}{d\xi} = -\,(C_j+\beta_j)\,, \quad \frac{d\,(T_2+\beta)}{d\xi} = -\,(T_2+\beta)\,.$$

Using the boundary conditions (5) we have

$$C_j = \left[\,(C_{jR}-C_{j\infty})\,\mathrm{e}^{-\xi} + C_{j\infty}\ \mathrm{e}^{-\xi_R} - C_{jR}\right] \Big/ (\mathrm{e}^{-\xi_R}-1)\,, \quad j = 1\,,\,2\,,\,3\,, \tag{8}$$

$$C_4 = C_{4\infty}\ \mathrm{e}^{-\xi}\,,$$

$$T_2 = \left[\,(T_{2R}-T_{2\infty})\,\mathrm{e}^{-\xi} + T_{2\infty}\ \mathrm{e}^{-\xi_R} - T_{2R}\right] \Big/ (\mathrm{e}^{-\xi_R}-1)\,. \tag{9}$$

If we ignore as a first approximation the change in $\rho_2 D$ with distance

$$\xi = \frac{(\rho_2 v)_R}{\rho_2 D}\,\frac{R^2}{r}\,, \quad \xi_R = \frac{(\rho_2 v)_R}{\rho_2 D}\,R \approx \frac{v_R R}{D}\,.$$

The density of the O_2 mass flux to the particle surface via molecules and via Stefan flow is equal to the total rate of the chemical reactions

$$j_{1R} = D\rho_{2R}\,\left.\frac{\partial C_1}{\partial r}\right|_R - (\rho_2 v)_R C_{1R} = \rho_{2R} C_{1R}\,(k_1+k_2)\,. \tag{10}$$

Using (8) and (10) we obtain the equation for determining ξ_R:

$$\left(1 + \frac{\mu_5}{\mu_1}\,\frac{k_1+2k_2}{k_1+k_2}\,C_{1\infty}\right)\mathrm{e}^{-\xi_R} - \frac{(D/R)}{k_1+k_2}\,\xi_R - 1 = 0\,. \tag{11}$$

We find the concentration of O_2 on the particle surface from (7):

$$C_{1R} = \xi_R \Big/ \left(\frac{\mu_5}{\mu_1}\,\frac{k_1+2k_2}{(D/R)}\right) \tag{12}$$

Using (6), (8), and (12) we find the concentrations of CO_2, CO, and N_2:

$$C_{2R} = C_{2\infty}\ \mathrm{e}^{-\xi_R} + \frac{\mu_2}{\mu_5}\,\frac{k_1}{k_1+2k_2}\,(1-\mathrm{e}^{-\xi_R})\,, \tag{13}$$

$$C_{3R} = C_{3\infty}\ \mathrm{e}^{-\xi_R} + \frac{\mu_3}{\mu_5}\,\frac{2k_2}{k_1+2k_2}\,(1-\mathrm{e}^{-\xi_R})\,, \tag{14}$$

$$C_{4R} = C_{4\infty}\ \mathrm{e}^{-\xi_R}\,.$$

We perform the analysis of the solutions (11). Let us introduce the function

$$\Phi\,(\xi) = \left(1 + \frac{\mu_5}{\mu_1}\,\frac{k_1+2k_2}{k_1+k_2}\,C_{1\infty}\right)\mathrm{e}^{-\xi} - \frac{D/R}{k_1+k_2}\,\xi - 1\,.$$

From

$$\frac{\partial}{\partial\xi}\,\Phi\,(\xi) < 0$$

it follows that $\Phi(\xi)$ is a monotonically decreasing function. Furthermore, its sign changes in the interval $(\xi_1,\ \xi_2)$ where

$$\xi_1 = 0\,, \quad \xi_2 = \ln\left\{ 1 + \frac{\mu_5}{\mu_1}\,\frac{k_1 + 2k_2}{k_1 + k_2}\,C_{1\infty} \right\}.$$

It follows that Eq. (11) always has one and only one solution.

As numerical calculations show, in many real cases $\xi_R < 1$. If we take $e^{-\xi_R} = 1 - \xi_R$ Eq. (11) has the solution

$$\xi_R = \frac{\mu_5}{\mu_1}\;\frac{(k_1 + 2k_2)\,C_{1\infty}}{(k_1 + k_2) + (D/R) + \dfrac{\mu_5}{\mu_1}(k_1 + 2k_2)\,C_{1\infty}}\,. \tag{15}$$

Then by substituting (15) into (11), we obtain, in explicit form, the relationship between C_{1R} and $C_{1\infty}$:

$$C_{1R} = C_{1\infty} \Big/ \left(1 + \frac{k}{(D/R)} + \frac{\mu_5}{\mu_1}\,\frac{k_1 + 2k_2}{(D/R)}\,C_{1\infty} \right), \quad k = k_1 + k_2\,. \tag{16}$$

The expansion

$$e^{-\xi_R} = 1 - \xi_R + \frac{1}{2}\xi_R^2\,.$$

is more accurate. Substituting it into (11), we find ξ_R:

$$\xi_R = \frac{B}{2A} + \sqrt{\left(\frac{B^2}{2A^2} - \frac{C}{A} \right)},$$

where

$$A = \frac{1}{2}\left[1 + \frac{\mu_5}{\mu_1}\,C_{1\infty}\left(1 + \frac{k_2}{k_1 + k_2} \right) \right];$$

$$B = \left[1 + \frac{\mu_5}{\mu_1}\,C_{1\infty}\left(1 + \frac{k_2}{k_1 + k_2} \right) + \frac{D/R}{k_1 + k_2} \right];$$

$$C = \frac{\mu_5}{\mu_1}\,C_{1\infty}\left(1 + \frac{k_2}{k_1 + k_2} \right).$$

Using the relations obtained we find the equations for the heat and mass flux densities:

$$Q_{\lambda\,\mathrm{st}} = Q_\lambda + Q_{\mathrm{st}} = \frac{\lambda_2}{R}\left(T_{2R} - T_{2\infty}\,e^{-\xi_R}\right)\frac{\xi_R}{1 - e^{-\xi_R}}\,, \tag{17}$$

$$j_{1R} = \rho_{2R}\,\frac{D}{R}\left(C_{1\infty}\,e^{-\xi_R} - C_{1R}\right)\frac{\xi_R}{1 - e^{-\xi_R}}\,. \tag{18}$$

Using the quadratic expansion of $e^{-\xi_R}$ we obtain the approximate equation for

$$Q_{\lambda\,\mathrm{st}} = \frac{\lambda_2}{R}\left(T_{2R} - T_{2\infty}\right)\left(1 + \frac{\xi_R}{2}\,\frac{(T_{2R} + T_{2\infty})}{(T_{2R} - T_{2\infty})} \right).$$

Or, in view of (15), by using the condition $T_{2R} = T_{1R} = T_1$ we have

$$Q_{\lambda\,\mathrm{st}} = \alpha\left(T_1 - T_{2\infty}\right)\left(1 + \frac{P_{\mathrm{st}}}{2\beta}\left(\frac{\sum\limits_{i=1}^{2} k_i + P_{\mathrm{st}}}{\beta} + 1 \right)^{-1}\left(\frac{T_1 + T_{2\infty}}{T_1 - T_{2\infty}} \right) \right), \tag{19}$$

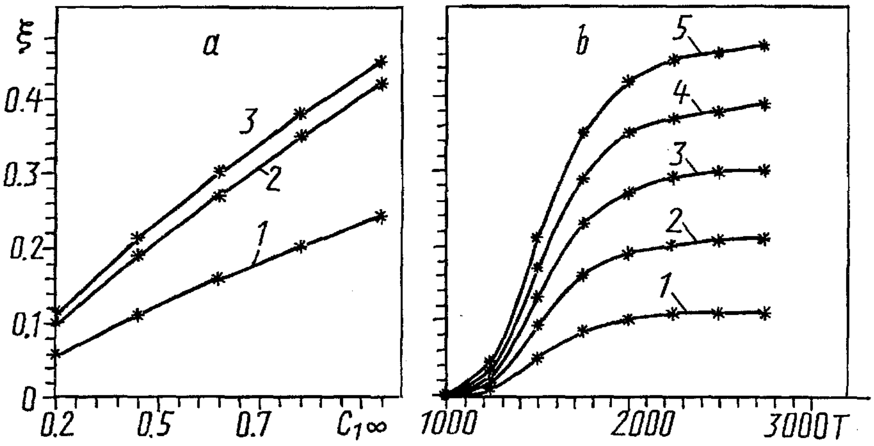

Fig. 1. Influence of the oxidant concentration and particle temperature on the Stefan flow velocity in two parallel reactions on the particle surface: a) T_{2R} = 200 K; 1) $R = 10^{-5}$; 2) 10^{-4}; 3) 10^{-3}; b) $R = 10^{-4}$; 1) $C_{1\infty} = 0.2$; 2) 0.4; 3) 0.6; 4) 0.8; 5) 1. T, K.

where $\alpha = \lambda_2/R$, $\beta = D/R$ are the heat and mass transfer coefficients;

$$P_{\text{st}} = \frac{\mu_5}{\mu_1}\left(\sum_{i=1}^{2} k_i + k_2\right) C_{1\infty}\ .$$

For the oxygen flux density we have

$$j_{1R} = \rho_{2R}\frac{D}{R}\left[(C_{1\infty} - C_{1R}) - C_{1\infty}\xi_R\right]\left(1 + \frac{\xi_R}{2}\right).$$

We find the gas density on the particle surface from the condition of an isobaric process

$$\rho_2 T_2 \sum_{j=1}^{4}\frac{C_j}{\mu_j} = \rho_{2R}T_{2R}\sum_{j=1}^{4}\frac{C_{jR}}{\mu_j} = \rho_{2\infty}T_{2\infty}\sum_{j=1}^{4}\frac{C_{j\infty}}{\mu_j}.$$

In view of (12)-(15) we have

$$\rho_{2R} = \rho_{2\infty}\frac{T_{2\infty}}{T_{2R}}\ \frac{1 + \dfrac{D/R}{k} + \dfrac{\mu_5}{\mu_1}\left(1 + \dfrac{k_2}{k}\right)C_{1\infty}}{1 + \dfrac{D/R}{k} + \dfrac{k_2^2}{k}\dfrac{C_{1\infty}}{\mu_1}\Big/\left(\sum_{j=1}^{4}\dfrac{C_{j\infty}}{\mu_j}\right)}.$$

As a result we obtain the equations for the heterogeneous reaction rate and Q_x:

$$W = j_{1R} = (k_1 + k_2)\,\rho_{2R}C_{1\infty}\left(\frac{\sum_{i=1}^{2} k_i + p_{\text{st}}}{\beta} + 1\right)^{-1}, \tag{20}$$

$$Q_x = (q_1k_1 + q_2k_2)\,\rho_{2R}C_{1\infty}\left(\frac{\sum_{i=1}^{2} k_i + p_{\text{st}}}{\beta} + 1\right)^{-1}. \tag{21}$$

An equation for $d(t)$ is obtained from the equality

$$-\frac{1}{2}\rho_1 \frac{d(d)}{dt} = (\Omega_1 k_1 + \Omega_2 k_2)\rho_{2R} C_{1\infty} \left(\frac{\sum_{i=1}^{2} k_i + p_{st}}{\beta} + 1 \right)^{-1}, \qquad (22)$$

where Ω_1 and Ω_2 are the stoichiometric coefficients for the (I) and (II) reactions.

We perform an analysis of the influence of temperature, oxidant concentration, and particle radius on the value of the Stefan flow. At low temperatures ($T < 1000$ K) the influence of the Stefan flow can be ignored. Figure 1 shows that as the temperature increases, ξ_R initially increases drastically and subsequently changes slightly for all values of oxidant concentration. This has to do with the original "work" of the Arrhenius exponent (kinetic regime) followed at high temperatures, by that of the power dependence (diffusion regime). As the oxidant concentration increases, the velocity of the Stefan flow increases as the particle radius increases. For $R > 100\ \mu$m, the Stefan flow changes slightly with particle size.

Therefore, we presented a physicomathematical model of the interrelated HMT and Stefan flow in two parallel reactions on the particle surface and analyzed the Stefan flow velocity as a function of temperature, oxidant concentration, and particle radius. Preliminary calculations of Eqs. (1) and (22) using (19) and (21) showed that taking into the Stefan flow enables us to explain the weak dependence of the combustion temperature on the gas temperature [1]. The equations obtained for Q_x, $Q_{\lambda\,\mathrm{st}}$, and chemical reaction rates enable us to determine the characteristics of stationary high- and low-temperature stable and critical states of a carbon particle in air.

NOTATION

T, temperature, K; t, time, sec; ρ, density, kg/m^3; c, specific heat, J/(kg·K); d, diameter; R, particle radius, m; λ, thermal conductivity coefficient, W/(m·K); ε, particle emissivity; v, Stefan flow velocity, m/sec; r, radial coordinate; C_j, relative mass concentration of the jth component; μ_j, molar weight, kg/mole; k_1, k_2, constants of the first and the second reaction rates, m/sec; k_{01} and k_{02}, preexponents; E_1, E_2, activation energies, J/mole; D, diffusion coefficient, m^2/sec; $\xi = v_R R/D$, dimensionless value of the Stefan flow velocity; Q_x, surface power of heat release, W/m^2; $Q_{\lambda\,\mathrm{st}}$, density of the heat flux via heat conduction and Stefan flow, W/m^2; Q_r, density of the heat flux via radiation; j_j, mass flux density; W, rate of the heterogeneous chemical reaction in O_2, kg/(m^2·sec). Indexes: 1, particle; 2, gas; w, wall; st, Stefan; ∞, infinitely distant; in, initial; R, on the particle surface; λ, by heat conduction; r, by radiation; $j = 1$, O_2; $j = 2$, CO_2; $j = 3$, CO; $j = 4$, N_2.

REFERENCES

1. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Moscow (1987).
2. V. V. Pomerantsev (ed.), Fundamentals of a Practical Theory of Combustion [in Russian], Leningrad (1986).
3. E. S. Golovina, High-Temperature Combustion and Gasification of Carbon [in Russian], Moscow (1983).
4. V. V. Kalinchak, S. G. Orlovskaya, and A. I. Kalinchak, Inzh.-Fiz. Zh., 62, No. 3, 436-442 (1992).
5. V. V. Kalinchak, S. G. Orlovskaya, and A. I. Kalinchak, Heat and Mass Transfer, MIF-92, Vol. 3, Minsk (1992), pp. 11-15.
6. S. G. Orlovskaya and V. V. Kalinchak, Fiz. Goreniya Vzryva, 26, No. 1, 115-118 (1990).
7. V. I. Babii and Yu. F. Kuvaev, Coal Dust Combustion and Calculation of a Coal Flame [in Russian], Moscow (1986).