

Mathematical Modeling of Multicomponent Nonisothermic Diffusion in the Process of the Thermal Decomposition of Ammonium Nitrate Melt in a Dispersed Flow¹

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Received May 23, 2016

Abstract—The kinetics of the heterogeneous process of the thermal decomposition of condensed substance particles with the formation of gaseous reaction products is considered using an example of the process of obtaining nitrous oxide via the thermal decomposition of the ammonium nitrate melt. A mathematical model has been obtained based on the methods of the thermodynamics of irreversible processes taking into account the thermal phenomena and the multicomponent composition of the reaction products. Using the methods of multicomponent hydrodynamics, expressions of crossed kinetic coefficients determined from the measured physical quantities have been obtained. An analysis was carried out for some particular cases of the process using the developed mathematical model.

Keywords: kinetics, heterogeneous chemical process, multicomponent nonisothermal diffusion, thermal diffusion, diffusion thermal conductivity, Stefan flow, thermal decomposition, dispersed stream, condensed substance, ammonium nitrate, nitrous oxide

DOI: 10.1134/S0040579518020045

INTRODUCTION

Most of the processes implemented in research practice and industry are based on heterogeneous chemical transformations. The multivariance of the problems of the kinetics of heterogeneous transformations is due to the variety of the phase state of the initial components and reaction products in heterogeneous interaction (gas–liquid, gas–solid, liquid–solid) and localization of the reaction (in one phase, in all phases, at the phase interface). The complexity of the problems of the kinetics of heterogeneous transformations is associated with the close interaction of chemical transformation proper and the transport phenomena both within and between the phases

In a number of heterogeneous chemical processes, the decomposition of condensed substance plays an important role, which is a particular case of gas–solid and gas–liquid systems, e.g., the combustion of solid fuel, propellants, the decomposition of ammonium nitrate in order to obtain the medical nitrous oxide, and the catalytic decomposition of liquid hydrazine.

The basic propositions of Onsager's theory [1] without reference to the specific mechanism of trans-

port phenomena include the following: the principle of microscopic reversibility, the theory of equilibrium fluctuations, the postulate on the relationship between spontaneous fluctuations and irreversible transport processes, and linear phenomenological transfer equations. The Onsager reciprocity relation only establishes the symmetry between the cross kinetic coefficients. In the general form, the phenomena of multicomponent nonisothermal transport are considered in the monograph [2]. We outlined the general approaches we have used for heat dissipation processes in the thermal decomposition of condensed substance in a dispersed stream, e.g., ammonium nitrate in the process of producing nitrous oxide, which introduces the following additional factors: (1) the decomposition process is nonstationary; (2) the particle size changes over time.

When the condensed substance is decomposed, the molecular mass and heat transfer between the phases causes additional flows, i.e., a convective flow due to the conversion of condensed substance to gaseous products, Stefan flow, flow caused by thermal diffusion, and flow due to diffusion thermal conductivity.

The aim of this work is to obtain a mathematical description of the process of thermal decomposition of a condensed substance on the basis of thermodynamics of multicomponent nonisothermal diffusion processes with all phenomena taken into account.

¹ The proposed publication is based on the materials of joint research under the guidance and with the direct participation of Professor V.S. Beskov (1937–2010) and is dedicated to his bright memory.

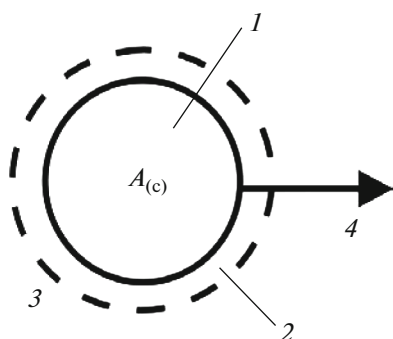


Fig. 1. Scheme of process of decomposition of condensed substance: (1) condensed component, (2) boundary layer, (3) bulk of gas phase, (4) mass flow of reaction products.

The above-presented discussion of possible phenomena at the decomposition of a condensed substance makes it possible to propose the following scheme for constructing a process model.

1. analysis of the process in a stationary boundary layer;
2. analysis of the nonstationary process of the decomposition of condensed substances;
3. determination of the conditions for reconciling the processes of stationary transport in the boundary layer and the nonstationary change in the state of the decomposed substance.

MATHEMATICAL MODEL OF THE PROCESS OF THE THERMAL DECOMPOSITION OF A CONDENSED SUBSTANCE

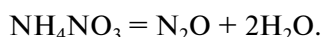
The decomposition of a condensed substance with the formation of gaseous products is described by the stoichiometric equation

$$A_{(c)} = \sum v_i R_{i(g)}.$$

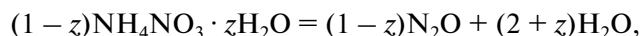
The scheme of the process is presented in Fig. 1.

The initial substance $A_{(c)}$ can be both single- and multicomponent.

An example of decomposition of single-component substance is the thermal decomposition of ammonium nitrate with the formation of nitrous oxide



In fact, in industrial conditions, a 92–96% solution of NH_4NO_3 is fed for decomposition. Therefore, the thermal decomposition of ammonium nitrate occurs with the release of hygroscopic moisture, and the decomposition reaction can be represented as follows:



where $(1 - z)\text{NH}_4\text{NO}_3 \cdot z\text{H}_2\text{O}$ is the substance to be decomposed (nitre) and z is the molar fraction of H_2O in nitre (in the case of decomposition of dry nitre $z = 0$).

The decomposition products are diverted from the surface to the surrounding volume, i.e., there is an interfacial mass transfer, from the surface of the condensed substance to the surrounding gas. The thermal effect of the decomposition reaction leads to a change in the temperature of surface of the decomposed substance and, as a consequence, to the occurrence of heat transfer between the phases. In many cases, interfacial transfer is associated with the molecular mechanism of transport through the boundary layer, i.e., the substance transfer is associated with transport by diffusion; heat transfer is associated with transport by thermal conductivity.

Mathematical Model of the Process of the Thermal Decomposition of Condensed Substances in the Boundary Layer

The flows of substance and heat are related to the concentration and temperature gradients are [2, 3]

$$j_i = -R \sum_{k \neq 0} \gamma_{ik} \frac{\text{grad} x_k}{x_k} - \gamma_{i0} \frac{\text{grad} T}{T^2}; \quad (1)$$

$$q = -\gamma_{00} \frac{\text{grad} T}{T^2} + \sum_i j_i H_i - R \sum \gamma_{0i} \frac{\text{grad} x_i}{x_i}. \quad (2)$$

The components of the right sides of Eqs. (1) and (2) are as follows:

$R \sum_{k \neq 0} \gamma_{ik} \frac{\text{grad} x_k}{x_k}$ is the diffusion of substances, $\gamma_{i0} \frac{\text{grad} T}{T^2}$ is thermal diffusion; $\gamma_{00} \frac{\text{grad} T}{T^2}$ is thermal conductivity, $R \sum_i \gamma_{0i} \frac{\text{grad} x_i}{x_i}$ is diffusion thermal conductivity, and $\sum_i j_i H_i$ is heat transferred by diffusion due to the difference in the thermal contents of diffusing substances.

In Eqs. (1) and (2), the kinetic coefficients γ_{ik} are not defined. Onsager's rule [1] establishes only the symmetry between the cross-kinetic coefficients as follows:

$$\gamma_{ik} = \gamma_{ki}.$$

We set the task using the methods of multicomponent hydrodynamics to obtain the values of cross-kinetic coefficients.

In the hydrodynamic representation of diffusion processes, the balance equation for the fluxes of substances in a multicomponent mixture in nonisothermic space is given in [2] as follows:

$$\begin{aligned} \text{grad} p_i &= \frac{(RT)^2}{P} \sum_{k \neq i} \frac{1}{D_{ik}} (c_i j_k - c_k j_i) \\ &+ \frac{M_i c_i}{\rho} \text{grad} P + \sum_{k \neq i} c_i c_k (M_i - M_k) \\ &\times \frac{d \ln \langle \varphi \rangle_{ik}}{d \ln T} \frac{RT}{\rho} \frac{\text{grad} T}{T}, \end{aligned} \quad (3)$$

where $\langle \varphi \rangle_{ik}$ is the function that characterizes the section of the collision of a pair of molecules of components i and k averaged by the distribution relative to velocity and linked with the thermal dependence of the diffusion coefficient, i.e.,

$$\frac{d \ln \langle \varphi \rangle_{ik}}{d \ln T} = -(2 - m_{ik}),$$

where m_{ik} in the equation of dependence of coefficient of mutual diffusion on temperature

$$D_{ik} = D_{0,ik} \left(\frac{T}{T_0} \right)^{m_{ik}} \frac{P_0}{P}.$$

($D_{0,ik}$ is determined at the temperature T_0 and pressure P_0).

In a boundary layer, we can accept that $P = \text{const}$ and $\text{grad} P = 0$, from which it follows that $x_i = p_i/P$, $c_i = p_i/RT = x_i P/RT$, $\rho = \sum_i c_i M_i$, $p_i = x_i P$.

Equation (3) can be reduced to the form

$$\begin{aligned} \text{grad} x_i &= \frac{RT}{P} \left[x_i \sum_k \frac{j_k}{D_{ik}} - j_i \sum_k \frac{x_k}{D_{ik}} \right] \\ &- \sum_k x_i x_k \frac{(M_i - M_k)(2 - m_{ik})}{\sum_i x_i M_i} \frac{\text{grad} T}{T}. \end{aligned} \quad (4)$$

It should be noted that, in an equation of form (4), summation can be made for all values k , including $k = i$. At $k = i$, the members under the sign \sum are identically equal to 0.

Solving Eq. (4) relative to j_i , we will obtain the equation for the flux of i th substance in the boundary layer as follows:

$$j_i = - \frac{\text{grad} x_i P}{RT \sum_k \frac{x_k}{D_{ik}}} - \frac{\sum_k x_i x_k \frac{(M_i - M_k)(2 - m_{ik})}{\sum_i x_i M_i} \frac{\text{grad} T}{T} \frac{P}{RT}}{\sum_k \frac{x_k}{D_{ik}}} + \frac{x_i \sum_k \frac{j_k}{D_{ik}}}{\sum_k \frac{x_k}{D_{ik}}}. \quad (5)$$

The effective diffusion coefficient averaged by the Wilkes's rule [2] is

$$D_i = \frac{1}{\sum_k \frac{x_k}{D_{ik}}}; \quad (6)$$

thermal diffusion relation for the i th component in a flux (thermal diffusion coefficient) is

$$k_{Ti} = \sum_k x_i x_k \frac{M_i - M_k}{\sum_i x_i M_i} (2 - m_{ik}); \quad (7)$$

the effective mass flow rate of the i th component directed normal to the surface and caused by the passing of reaction is

$$v_i = \frac{\sum_k \frac{j_i}{D_{ik}}}{\sum_k \frac{x_k}{D_{ik}}}. \quad (8)$$

A hydrodynamic representation of the diffusion processes made it possible to obtain the relation for mass flow rates of substances j_i as follows:

$$j_i = - \frac{PD_i}{RT} \text{grad} x_i - k_{Ti} \frac{PD_i}{RT} \frac{\text{grad} T}{T} + x v_i. \quad (9)$$

To obtain the heat-balance equation, let us turn to the thermodynamic theory. Eq. (9) must be reduced to the form of Eq. (1) and, using Onsager's rule [1] on the symmetry of the kinetic coefficients, to obtain the kinetic coefficients of Eq. (2).

When Eq. (3) is summarized, we obtain

$$\sum_i \text{grad} p_i = \text{grad} P = 0,$$

which indicates the linear dependence of these equations.

In order for the system of equations to be definite, it is necessary to choose a frame of reference. The center-of-mass system was used in [4], since, in the catalytic process, all reagents are in the gas phase and their total mass does not change. In the thermal decomposition of a condensed substance, only the reaction products are in the gas phase and, for this process, it is better to use a laboratory reference system by assuming that the surface on which the decomposition reaction of the substance is stationary. In this case, the total flux of all components from the surface is constant, i.e.,

$$\sum_i j_i = r \sum_i v_i. \quad (10)$$

The flow of the i th component is linked with a rate r by the relation

$$j_i = v_i r. \quad (11)$$

Since there are no chemical transformations in the boundary layer, the fluxes of reaction products j_i formed on the surface of the condensed component are stationary in the stationary regime throughout the boundary layer; therefore, the ratio (11) can be assumed for the entire boundary layer.

After a series of transformations, the equation of the flux of the i th component is obtained in the form of Eq. (1):

$$j_i = -\frac{P}{RT} \sum_l \frac{v_l}{v_i} \sum_l \bar{D}_l x_l \frac{\text{grad} x_l}{x_l} - \frac{P}{R} \sum_l \frac{v_l}{v_i} \sum_l \bar{D}_l k_{Tl} \frac{\text{grad} T}{T^2}, \quad (12)$$

where

$$\bar{D}_i = \frac{D_i}{\left(1 - \frac{D_i x_i}{v_i} \sum_k \frac{v_k}{D_{ik}}\right)}.$$

Now, comparing Eqs. (12) and (1), we can obtain the relation for undefined kinetic coefficients of Eq. (2)— γ_{0i} .

According to Onsager's principle of reciprocity, the phenomenological coefficients for cross-effects satisfy the symmetry condition

$$\gamma_{0i} = \gamma_{i0},$$

from which we obtain

$$\gamma_{0i} = \frac{P}{R} \sum_l \frac{v_l}{v_i} \sum_l \bar{D}_l k_{Tl}.$$

In [2], it is determined that

$$\gamma_{00} \frac{\text{grad} T}{T^2} \equiv \lambda \text{grad} T$$

as heat flux due to the thermal conductivity of gas. Taking this into account, we transformed heat-balance equation (2) into the form

$$q = -\lambda \text{grad} T + \sum_i j_i H_i - \sum_l \frac{P}{v_l} \sum_l \left[v_l \frac{\text{grad} x_l}{x_l} \sum_l \bar{D}_l k_{Tl} \right]. \quad (13)$$

Thus, substance and heat fluxed in a boundary level are described by the Eqs. (12) and (13), the coefficients in which

$$D_i = \frac{1}{\sum_k \frac{x_k}{D_{ik}}}, \quad (14)$$

$$k_{Ti} = \sum_k x_i x_k \frac{M_i - M_k}{\sum_i x_i M_i} (2 - m_{ik}), \quad (15)$$

$$v_i = \frac{\sum_k j_k}{\sum_k \frac{x_k}{D_{ik}}}, \quad (16)$$

$$\bar{D}_i = \frac{D_i}{1 - \frac{D_i x_i}{v_i} \sum_k \frac{v_k}{D_{ik}}} \quad (17)$$

are expressed through the measured physical values.

Next, we obtain an expression for the heat transported with the flows of substances $\sum_i j_i H_i$. Let us take the reference temperature of the heat content T^* . Then, the heat content of each component $H_i(T)$ is divided into two terms, i.e., constant and temperature-dependent T , as follows:

$$H_i(T) = H_i(T^*) + \bar{C}_p(T - T^*),$$

and

$$\begin{aligned} & \sum_i j_i H_i(T) \\ &= \sum_i j_i H_i(T^*) + \sum_i j_i \bar{C}_p(T - T^*). \end{aligned} \quad (18)$$

Heat flow $\sum_i j_i H_i(T^*)$ is the energy released when reaction products are formed at a temperature T^* . It is equal to the change in enthalpy in the formation of gaseous products and is reversed in the sign of the rate of heat release of the decomposition reaction. The second term in Eq. (18) is the physical heat carried by the flows as the temperature of the flows varies from T^* to T . Thus,

$$\sum_i j_i H_i = -Q_p(T^*) r(T_s) + (T - T^*) \sum_i \bar{C}_{pi} j_i. \quad (19)$$

In the chosen reference frame, the reaction rate is determined by the surface temperature T_s . The average integral heat capacity is

$$\bar{C}_p = \frac{1}{T - T^*} \int_{T^*}^T C_p(T) dT.$$

The thermal effect of the reaction is determined at the temperature of the reference point T^* , and the temperature dependence of the enthalpy on the temperature $H(T)$ is determined by the dependence and deviation of the temperature T from T^* . If we neglect the change in the specific heat from the temperature and assume that it does not depend on the composition, then Eq. (19) takes the form

$$\begin{aligned} & \sum_i j_i H_i \\ &= -\left[Q_p(T^*) - C_p(T - T^*) \sum_i v_i \right] r(T_s). \end{aligned} \quad (20)$$

Thus, the process of thermal decomposition of condensed substance is described by the equations

$$j_i = -\frac{PD_i}{RT} \text{grad} x_i - \frac{PD_i}{RT} k_{Ti} \frac{\text{grad} T}{T} + v_i x_i, \quad (21)$$

$$q = -\lambda \text{grad} T - Q_p(T^*)r(T_s) + (T - T^*) \times \sum_i (C_{pi} j_i) - \sum_i v_i \sum_l (\overline{D_l} k_{Ti}) \sum_i \left(v_i \frac{\text{grad} x_i}{x_i} \right), \quad (22)$$

$$D_i = \frac{1}{\sum_k \frac{x_k}{D_{ik}}}, \quad (23)$$

$$v_i = D_i \sum_k \frac{j_k}{D_{ik}}, \quad (24)$$

$$k_{Ti} = x_i \sum_l \left[x_k \frac{M_i - M_k}{\sum_l x_l M_l} (2 - m_{ik}) \right], \quad (25)$$

$$\overline{D_i} = \frac{D_i}{1 - x_i \frac{D_i}{v_i} \sum_k \frac{v_k}{D_{ik}}}. \quad (26)$$

For a 1D flow from the flat surface of a condensed component,

$$\text{grad} x = \frac{dx}{dl} \text{ and } \text{grad} T = \frac{dT}{dl}, \quad (27)$$

where l is the coordinate normal to the surface of the phase boundary.

Taking into account Eq. (27), we transform Eqs. (21) and (22) and transfer them to a form that shows the change in concentration $\frac{dx}{dl}$ and temperature $\frac{dT}{dl}$ in the boundary layer as follows:

$$\frac{P}{RT} D_i \frac{dx}{dl} = v_i r(T_s) - \frac{P}{RT} D_i k_{Ti} \frac{dT}{dl} + v_i x_i, \quad (28)$$

$$\lambda \frac{dT}{dl} = -[Q_p(T^*) + (T - T^*) \overline{C_p}] r(T_s) - \sum_i \frac{P}{v_i} \sum_l \overline{D_l} k_{Ti} \sum_i \left(\frac{v_i}{x_i} \frac{dx}{dl} \right) - q. \quad (29)$$

The thickness of the boundary layer at the surface of the condensed component is δ , from which we determine the heat-transfer coefficients α and mass transfer β_i as follows:

$$\alpha = \frac{\lambda}{\delta} \text{ and } \beta_i = \frac{P}{RT} \frac{D_i}{\delta}. \quad (30)$$

Determining $\overline{C_p} = \sum_i v_i \overline{C_{pi}}$ as the average heat capacity of the reaction products formed from 1 mol of the initial substance, we obtain equations that describe

the process in the boundary layer from its dimensionless coordinate $\xi = l/\delta$ as follows:

$$\beta_i \frac{dx}{d\xi} = -v_i r(T_s) - \beta_i \frac{k_{Ti}}{T} \frac{dT}{d\xi} + v_i x_i, \quad (31)$$

$$\alpha \frac{dT}{d\xi} = q - [Q_p(T^*) - (T - T^*) \overline{C_p}] r(T_s) - \sum_i \frac{P}{v_i} \sum_l \left[\frac{v_i}{x_i} \frac{dx_i}{dl} \sum_l \overline{D_l} k_{Ti} \right]. \quad (32)$$

Here,

$$\overline{D_i} = \frac{\beta_i}{1 - \frac{x_i}{v_i} \sum_k \frac{v_k}{D_{ik}}} = \frac{\beta_i}{1 - \frac{x_i}{v_i} D_i \sum_k \frac{v_k}{D_{ik}}}.$$

The boundary conditions for Eqs. (31)–(32) are determined by the following conditions (concentration and temperature) in the bulk:

$$\text{at } \xi = 1, \quad x = x_0; \quad T = T_0. \quad (33)$$

Thermal Phenomena during the Thermal Decomposition of a Condensed Substance

The total heat flux q in Eq. (22) is the heat removed from the surface by radiation and direct contact with bodies that do not participate in the reaction. During the thermal decomposition of ammonium nitrate, there are no bodies that do not participate in the reaction. However, the decomposition surface and the boundary layer enter the considered process structure, the decomposition surface being directly in contact with the volume of the decomposable substance. Thus, the body that does not participate in the reaction is actually the decomposable condensed component, and the reaction heat is not only diverted from the surface to the gas volume, which is described by the second and third terms on the right side of Eq. (22), but also goes to heating the particle itself, represented by the total heat flux q .

Let us suppose that the entire particle is heated uniformly throughout the volume. The change in the temperature of the particle of the condensed component T_c and the heat flux q from the unit surface going to heat the particle are linked with the heat balance as follows:

$$q = \rho_c \frac{V_c}{S_c} C_c \frac{dT_c}{dt}. \quad (34)$$

If we take into account the heating of the particle in the form of a ball in depth, then the temperature change along the radius r of the particle is described by the equation of thermal conductivity

$$\lambda_c \left[\frac{\partial^2 T_c}{\partial r^2} + \frac{2}{r} \frac{\partial T_c}{\partial r} \right] = C_c \frac{\partial T_c}{\partial t}. \quad (35)$$

The boundary conditions are follows:

$$\begin{aligned} \text{at } r_c = 0, \frac{\partial T_c}{\partial r} = 0; \text{ at } r_c = R_0, \lambda_c \frac{\partial T_c}{\partial r} = q; \\ \text{at } t = 0, T(r_c) = T_{\text{in}}. \end{aligned} \quad (36)$$

Equations (34) or (35) with the boundary conditions (36) complement boundary-layer Eqs. (28)–(29).

Analysis of the Process of the Decomposition of a Condensed Substance: Decomposition into a Volume of Gas Consisting of Reaction Products

Let us consider a particular case of the process of the decomposition of condensed substance. Let us assume that the composition of the gas in the volume is only formed from the reaction products, and the ratio of the product concentrations will correspond to their stoichiometric ratio in the decomposition reaction as follows:

$$x_i = \frac{v_i}{\sum_i v_i}. \quad (37)$$

We transform the second term in the denominator of Eq. (26) as follows:

$$\begin{aligned} x_i \frac{D_i}{v_i} \sum_k \frac{v_k}{D_{ik}} &= D_i \frac{v_i}{v_i \sum_i v_i} \sum_k \frac{v_k}{D_{ik}} \\ &= D_i \sum_k \frac{v_k / \sum_i v_i}{D_{ik}} = D_i \sum_k \frac{x_k}{D_{ik}} = D_i \frac{1}{D_i} = 1. \end{aligned}$$

With this value of the second term in the denominator of Eq. (26), $\bar{D}_i \rightarrow \infty$. In this case, the heat-balance equation (34) will retain meaning if there is no concentration gradient, i.e., $\text{grad} x = 0$. Taking into account the relationship $j_i = v_i r(T_s)$, Eqs. (29) and (30) will be

$$v_i r(T_s) = v_i x_i - \frac{P}{RT} D_i k_{Ti} \frac{\text{grad} T}{T}, \quad (38)$$

$$q = -\lambda \text{grad} T + \sum_i j_i H_i. \quad (39)$$

The gaseous products of the reaction are diverted from the surface of the condensed component due to the hydrodynamic flows that arise from the transition of the initial condensed material to gaseous products (the first term in Eq. (38)) and the larger volume of gases at the surface of the condensed material heated by the heat of the chemical reaction (second term in the right side of Eq. (38)). In Eq. (39), the first term on the right side describes the heat flux between the surface and the volume due to the thermal conductivity of

the gaseous medium, the second is the heat flux removed from the reaction products formed.

Since all of the products formed in the reaction are diverted from the surface, and the concentration does not depend on their concentration, we can further consider only the heat balance Eq. (39). For a plane boundary layer, the heat-balance equation takes the form

$$\alpha \frac{dT}{d\xi} = -[Q_p(T^*) - \bar{C}_p(T - T^*)]r(T_s) - q. \quad (40)$$

Analysis of the Process of the Decomposition of the Particle of Condensed Component into Two Gaseous Products within a Boundary Layer

Condensed substance A_c decomposes into gaseous products R and S :



In the gas phase, other substances are not presented, i.e., condensed substance is surrounded by a two-component gas phase that consists only of decomposition products.

In the process of decomposition, the initial substance is consumed, and if it was in the form of a round drop, then the change in the amount of the condensed component n as a result of its decomposition is described by the equation

$$\frac{dn}{dt} = S_c r(T_s), \quad (41)$$

where $S_c = \pi d_c^2$ is the surface area of droplet and $dn = \frac{\rho}{M} S_c d \left(\frac{d_c}{2} \right)$ is the change of quantity of condensed component in droplet.

The velocity of the change in the size of droplet d_c is

$$\frac{dd_c}{dt} = 2 \frac{M}{\rho} r(T_s). \quad (42)$$

On Agreement between Models of the Process in the Boundary Layer and the Changes in the State of a Condensed Component

Equations (39)–(40) describe a stationary process in the system of surface of condensed substance-a boundary layer. Equations (40)–(41) of particle heating and Eq. (42), which describe changes in particle size, represent nonstationary processes.

Strictly speaking, models of particular processes of the decomposition of a condensed substance do not match in their temporal characteristics. To be able to share these equations it is necessary to determine the characteristic times for staging particular processes, i.e., if the characteristic time of staging one process is much shorter than the other, then the first will be in an almost stationary state when another process takes

place. Of course, the stationary state will change with the change in conditions due to the slower process. In this case, it is customary to say that the first process is quasi-stationary with respect to the other, and it is justified to use the stationary model of the first process and the nonstationary model of the other.

Let us estimate the characteristic times of staging the partial processes of the decomposition of condensed substance. The characteristic time of staging τ_{BL} of the concentrations in a boundary layer of δ thickness in which the transfer of substance is carried out by diffusion (diffusion coefficient D) as follows:

$$\tau_{BL} = \delta^2/D.$$

The ratio $D/\delta = \beta$ is the mass-transfer coefficient determined from the Nusselt number

$$Nu = \beta d_c/D.$$

The minimum value of the Nusselt number (particle in a fixed medium) is $Nu = 2$, from which we have

$$\delta = d_c/2, \quad (43)$$

and

$$\tau_{BL} = d_c^2/(4D). \quad (44)$$

The characteristic time of staging of temperature τ_t during particle heating is determined by the size (radius $r_c = d_c/2$), heat capacity, and thermal conductivity as follows:

$$\tau_t = r_c^2 C_{\text{particle}}/\lambda. \quad (45)$$

Based on the reference data [5–7], it is possible to estimate the value of D for gases and C_{particle} and λ for liquids as follows:

$$D \approx 0.1\text{--}1 \text{ cm}^2/\text{s}; \quad C_{\text{particle}} \approx 0.5\text{--}1 \text{ cal}/(\text{cm}^3 \text{ }^\circ\text{C}); \\ \text{and } \lambda \approx 0.2\text{--}0.5 \text{ kcal}/(\text{m}^2 \text{ h } ^\circ\text{C}).$$

Based on these estimates and Eqs. (43) and (45), we obtain

$$\tau_{BL} \approx (0.25\text{--}2.5)d_c^2 [\text{s}]; \quad \tau_t \approx (400\text{--}1500)d_c^2 [\text{s}].$$

It follows from a comparison of the values of τ_{BL} and τ_t that the characteristic time of transfer in a boundary layer τ_{BL} is more than two orders higher than the characteristic time of particle warming up τ_t . Thus, this process in a boundary layer can be considered quasi-stationary with respect to the warming up of particles.

A comparison of the characteristic time of process staging in the boundary layer and the change in the particle size of the condensed substance showed that the rate of change in the concentration distribution in the boundary layer is more than two orders of magnitude greater than the rate of change in the degree of conversion of the condensed component. Therefore, the process in the boundary layer can be regarded as quasi-stationary with respect to the transformation of the decomposable component. The estimates are used

to justify the possibility of using the obtained stationary model of the process in the boundary layer and the nonstationary models for heating the particle of the condensed component and its transformation.

Isothermic Process

In an isothermal boundary layer, $dT/d\xi = 0$, so we analyze the process using the equation of mass balance. For a two-component mixture, the process parameters take the following form:

$$D_{ij} = D_{12} = D_{21} \equiv D; \quad D_1 = D_2 \equiv D;$$

$$x_1 \equiv x; \quad x_2 = 1 - x;$$

$$j_1 = v_1 r(T); \quad j_2 = v_2 r(T).$$

It follows from Eq. (28) that, for $i = 1$,

$$D \frac{dx}{d\xi} = -v_1 r(T) + (v_1 + v_2) r(T) \quad (46) \\ = -r(T) [(v_1 + v_2)x - v_1].$$

In the case of the stoichiometric composition of the gas phase in the bulk ($\xi = 1$),

$$x = \frac{v_1}{v_1 + v_2}, \quad (v_1 + v_2)x = v_2.$$

In this case, $dx/d\xi = 0$ is the composition of gaseous products on the surface, which is also stoichiometric. The retraction of the reaction products from the surface is only carried out by the convective flow, which is equal to the rate of the formation of gaseous products as follows:

$$j_1 = v_1 r(T) \text{ and } j_2 = v_2 r(T).$$

When the composition of the gas mixture in the volume is nonstoichiometric, one can obtain a concentration distribution on the surface, integrating Eq. (46) over the thickness δ of the boundary layer as follows:

$$\ln \frac{1 - \sum_v x_0}{1 - \sum_v x_s} = \frac{\sum_v v}{\beta} r. \quad (47)$$

Nonisothermic Process

Analysis of the process in the nonisothermal boundary layer is carried out according to the equations of mass and heat balances. In addition to the process parameters described above, there are also the following thermal diffusion coefficients k_{Ti} :

$$k_{T1} = x(1-x) \frac{M_1 - M_2}{v_1 M_1 + v_2 M_2} (2 - m) \equiv k_T, \\ k_{T2} = -k_{T1}.$$

Here, $v_1 M_1 + v_2 M_2$ is the molecular weight of the condensed component.

The parameters of the heat-balance equation are

$$\bar{D}_1 = \frac{D}{1 - x \frac{v_1 + v_2}{v_1}}; \bar{D}_2 = \frac{D}{1 - (1 - x) \frac{v_1 + v_2}{v_2}}.$$

In the right-hand side of Eq. (32), the second and last terms are equal to zero. Now, Eq. (32) takes the form

$$\alpha \frac{dT}{d\xi} = -[Q_p(T^*) - (T - T^*) \sum (v_i \bar{C}_{pi})] r(T_s). \quad (48)$$

With an insignificant change in the heat capacity with a change in temperature, we can assume $\bar{C}_{pi} = \text{const}$. Then, taking into account Eq. (20), we reduce Eq. (48) to the form

$$T_s - T_0 = \frac{Q_p r(T_s)}{\alpha}. \quad (49)$$

The temperature gradient in the boundary layer changes the flow of gaseous reagents due to thermal diffusion represented in Eq. (28) by the second term. Equation (48) is supplemented by the equation

$$\frac{dx}{d\xi} = -\frac{RT}{P\beta} \left[1 - \sum \frac{v}{v_1} x \right] r(T_s) - \frac{k_T}{T} \frac{dT}{d\xi}. \quad (50)$$

Analysis of the Influence of Thermal Phenomena on the Process of the Decomposition of a Condensed Substance: Thermodiffusion Flow

During the thermal decomposition of condensed substance, a temperature difference exists between the surface of the solid and the volume of the gas phase. The reaction rate has a direct effect on the magnitude of the temperature gradient; as the process speed increases (see Eq. (49)), the difference in the temperature of the surface and the volume of the gas also increases.

Under these conditions, a concentration gradient appears in the boundary layer from its dimensionless coordinate $\xi = l/\delta$, which is caused by thermal diffusion as follows:

$$\frac{dx}{d\xi} = -\frac{k_T}{T} \frac{dT}{d\xi}. \quad (51)$$

The value of the coefficient of thermal diffusion is calculated by the formula

$$k_T = x(1 - x) \frac{M_1 - M_2}{v_1 M_1 + v_2 M_2} (2 - m). \quad (52)$$

As can be seen from Eq. (52), the difference in the molecular weights of the components makes the main contribution to the value of the coefficient of thermal diffusion, while Eq. (51) gives the temperature drop between the surface and the volume of the gas phase.

CONCLUSIONS

An analysis of the mathematical model of the thermal decomposition of a particle of condensed substance shows that the Stefan and thermodiffusion fluxes are the determining factors in the kinetics of the heterogeneous process. It has been determined that the process in the boundary layer can be considered quasi-stationary with respect to the transformation of the decomposable component, which allows the use of the obtained stationary model of the process in the boundary layer and the nonstationary models for heating the particle of the condensed component and its transformation.

NOTATION

C_c	average mass heat capacity of condensed component
\bar{C}_{pi}	average integral heat capacity of i th component in a temperature range $T - T^*$
c	concentration
D	diffusion coefficient
D_i	diffusion coefficient of i th component in mixture
D_{ic}	binary diffusion coefficient
d_c	particle diameter of condensed component
$H_i(T^*)$	heat content of i th component at temperature T^*
j_i	diffusion flow of i th substance
M_i	molecular weight of i th component
m_{ic}	coefficient of temperature dependence of diffusion coefficient
P	pressure, Pa
Q_p	heat effect of reaction, kJ/mol
$Q_p(T^*)$	heat effect of reaction, determined at temperature T^*
q	full heat flux
R	universal gas constant, J/(mol K)
r	coordinate by the radius of particle
$r(T)$	rate of decomposition of initial substance
r_c	current radius of particle
S_c	surface of decomposition of particle of condensed component
T	temperature, K
T_c	temperature of particle of condensed component
T_{in}	initial temperature of particle of condensed component
T_{Π}	temperature of surface of condensed substance
T_0	temperature in the bulk of gas phase
t	time, s
V_c	volume of particle of condensed component

x_i, x_k	molar fractions of i th and k th component in mixture	c	condensed component
x_0, x_s	concentration of component R in volume and on the surface	BL	boundary layer
		particle	particle of condensed component

α	heat-transfer coefficient through the boundary layer
β	mass-transfer coefficient through the boundary layer, $\beta = D/\delta$
δ	thickness of the boundary layer
γ_{ik}	kinetic coefficients, symmetric by the indices i, k ($i, k \neq 0$)
λ	thermal conductivity
λ_c	thermal conductivity of condensed component
ν_i	stoichiometric coefficient of i th component
$\sum_i \nu_i$	total number of moles of gaseous products, formed from one mole of initial substance
ξ	dimensionless coordinate in boundary layer
ρ	density, g/m ³
τ	dimensionless time
$\langle \phi \rangle_{ik}$	function, characterizing the section of collision of pair of molecules of components i and k , averages by the distribution of velocities of molecules
Nu	Nusselt number

SUBSCRIPTS AND SUPERSSCRIPTS

0	heat values
i, j	numbers of components

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Translated by A. Bannov