

Simulation of the Kinetics of Complex Heterogeneous Catalytic Reactions under Diffusion Limitations

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Abstract—A method is suggested for determining kinetic parameters of arbitrary complex heterogeneous catalytic reactions under conditions such that the reaction rate is significantly affected by heat and mass transfer to and in the catalyst pellets. Linear relationships are established between the concentrations of the key and dependent reactants (diffusion stoichiometry relationships) and between temperature and the concentrations of the key components. A solution procedure is suggested for the problems involved in the determination of kinetic parameters for reactions proceeding under diffusion limitations. The procedure is illustrated by analysis of data earlier reported for steam methane reforming over a nickel catalyst.

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Finding the parameters of kinetic equations (kinetic parameters) is a necessary and important step in the construction of a kinetic model for a complex heterogeneous catalytic reaction (HCR). The resulting kinetic model can be used in the design and optimization of industrial-scale reactors and chemical technologies. The kinetic parameters for a chosen kinetic model are most often derived from the results of experiments carried out under steady-state conditions in a perfectly mixed gradientless or plug flow reactor. For this purpose, it is preferable to use experimental data obtained under kinetic control, when the reaction rate is independent of heat and mass transfer near the surface of the catalyst pellet and in the pellet bulk.

However, in kinetic studies, it is often impossible to conduct an HCR in the kinetic regime because of the high activity of the catalyst or high experimental temperature and pressure (which are dictated by the researcher's wish to establish kinetic relationships for process conditions imitating real technology). Therefore, there is a need for a model, mathematical tools, and software for determining the kinetic parameters of complex HCRs proceeding under diffusion limitations on the catalyst pellet. As will be demonstrated below, solving this problem is a complicated iterative process that includes hierarchical sequential solution of optimization problems, solution of sets of ordinary differential equations, and solution of sets of partial differential equations. This procedure requires methods and algorithms taking into account both the physics of the problem treated at a given solution stage and the specific features of the algorithms to be employed at the other levels of solving the general problem.

MATHEMATICAL MODELS

For definiteness, we will assume that the kinetic experiments have been carried out in an isothermal plug flow reactor. The mathematical model of this reactor is defined by the following set of ordinary differential equations (ODEs):

$$\frac{d\mathbf{W}_k}{dV} = \mathbf{r}_k^{\text{obs}}(\mathbf{P}, T, \mathbf{k}), \quad (1)$$

where \mathbf{W}_k is the vector of the flows of the key components (mol/s); V is the current value of the bed volume (m^3), which is used as the longitudinal coordinate; $\mathbf{r}_k^{\text{obs}}$ is the vector of observed reaction rates with respect to the key component concentrations ($\text{mol m}^{-3}(\text{bed}) \text{ s}^{-1}$); \mathbf{P} is the vector of the partial pressures of the reaction participants (bar); T is the temperature (K); and \mathbf{k} is the vector of kinetic parameters. For ODE set (1), we have to solve a Cauchy problem in which all component flows at the reactor inlet ($V = 0$) are specified.

The flows of the nonkey (dependent) components of the HCR in a cross section of the reactor are expressed in terms of the key component flows in this cross section and the flows of all components at the reactor inlet, taking into account the reaction stoichiometry [1]. The partial pressure of the i th reactant is $P_i = PW_i/W$, where P is the total pressure and W is the total flux. For the sake of simplicity, we will assume that the pressure drop across the reactor length is negligible.

The kinetic parameters (preexponential factors of the rate or equilibrium constants of elementary steps and the activation energies of these steps or heats of

adsorption) can be found, for example, by minimizing the following objective function:

$$S = \sum_{i=1}^{N_{\text{exp}}} \sum_{j=1}^{N_k} [(y_{i,j}^{\text{calc}} - y_{i,j}^{\text{exp}})/y_{i,j}^{\text{exp}}]^2. \quad (2)$$

In Eq. (2), $y_{i,j}^{\text{exp}}$ may be, e.g., the average formation rate of the j th key component in the i th experiment (i.e., the ratio of the difference between the outlet and inlet flows to the volume of the catalyst bed), $y_{i,j}^{\text{calc}}$ may be the same rate calculated using Eq. (1) for the conditions of the i th experiment, N_{exp} is the number of experiments, and N_k is the number of key components. The minimization problem can be solved with or without imposing constraints on the parameters being fitted or on the functions of these parameters.

The processes occurring on a catalyst pellet are conventionally described using a quasi-homogeneous model in which the pellet is viewed as some homogeneous medium and effective values of the diffusion, heat transfer, and mass transfer coefficients and heat conductivity are used [2, 3]. Mass transfer in the pellet is described in terms of the Stefan–Maxwell equation [3–5] or equations following from Fick's law [2, 7, 8]. The difference between these approaches has been discussed in the literature (see, e.g., [4–6]). It is believed that the former is physically better substantiated and is more general; however, no differences between these approaches arise in mass transfer calculations [4, 5].

Because solving the inverse problem examined is computation-intensive, we will take the approach based on Fick's law, which is computationally simpler. It will be assumed that the effective in-pellet diffusion coefficients are constant and can be calculated provided that the composition and temperature of the gas mixture near the pellet surface are known. The coefficients of mass and heat transfer to the pellet surface at a given point in the reactor are derived from the composition and temperature of the gas mixture in the flow core [7, 8].

We will use the following expression of Fick's law (Eq. (3)) and Fourier's laws (Eq. (4)):

$$-D_i^* \nabla C_i = \mathbf{J}_i, \quad i = 1, \dots, N_t, \quad (3)$$

$$-\lambda^* \nabla T = \mathbf{J}_T, \quad (4)$$

where C_i is the concentration of the i th component (mol/m^3), T is absolute temperature (K), D_i^* is the effective diffusion coefficient of the i th component (m^2/s), \mathbf{J}_i is the flux of the i th component in the pellet bulk ($\text{mol} \text{ m}^{-2} \text{ s}^{-1}$), λ^* is the effective heat conductivity of the pellet ($\text{W} \text{ m}^{-2} \text{ K}^{-1}$), \mathbf{J}_T is the heat flux in the pellet ($\text{W} \text{ m}^{-2} \text{ s}^{-1}$), and N_t is the total number of reactants. For definiteness, we will assume that the pellet is spherical and the radial coordinate axis is directed from the pellet center ($r = 0$) to the pellet surface ($r = a$). The laws of mass and energy conservation will be written as

$$\text{div} \mathbf{J}_i = r_i, \quad i = 1, \dots, N_t, \quad (5)$$

$$\text{div} \mathbf{J}_T = \sum_{j=1}^{N_r} (-\Delta H_j) R_j. \quad (6)$$

In Eq. (6), it is assumed that some basis set of reaction routes is chosen (the number of independent routes is N_r), R_j is the reaction rate for the j th route ($\text{mol} \text{ m}^{-3} \text{ s}^{-1}$), r_i is the formation rate of the i th component ($\text{mol} \text{ m}^{-3} \text{ s}^{-1}$), and $-\Delta H_j$ is the heat of the overall j th-route reaction (J/mol). In Eqs. (5) and (6) and hereafter, all rates pertaining to effects on the catalyst pellet will refer to a unit volume of the pellet.

Equations (3)–(6) lead to the following set of $N_t + 1$ second-order differential equations describing heat and mass transfer in the catalyst pellet:

$$D_i^* \Delta C_i + r_i = 0, \quad i = 1, \dots, N_t, \quad (7)$$

$$\lambda^* \Delta T + \sum (-\Delta H_j) R_j = 0. \quad (8)$$

Since the flows of all components and heat at the pellet center are zero, the set of equations (7) and (8) should satisfy the following boundary conditions:

$$\left. \frac{dC_i}{dr} \right|_{r=0} = 0, \quad \left. \frac{dT}{dr} \right|_{r=0} = 0. \quad (9)$$

The problem to be solved can be either internal-diffusion or external-diffusion, depending on the boundary conditions on the outer surface of the pellet.

If the component concentrations and temperature on the outer surface of the pellet are equal to those in the reactant flow core,

$$C_{is} = C_{ib}, \quad T_s = T_b, \quad (10)$$

then we will have an internal-diffusion problem. If the flows of all components and heat into the pellet bulk are equal to the respective flows from the flow core to the pellet surface, then

$$-D_i^* \left. \frac{dC_i}{dr} \right|_{r=a} = K_{mi} (C_{is} - C_{ib}), \quad (11)$$

$$-\lambda^* \left. \frac{dT}{dr} \right|_{r=a} = K_T (T_s - T_b), \quad (12)$$

and we have an external-diffusion problem. In Eqs. (11) and (12), K_{mi} and K_T are, respectively, the i th component mass transfer coefficient (m/s) and the flow core-to-pellet surface heat transfer coefficient ($\text{W} \text{ m}^{-2} \text{ K}^{-1}$). The subscript s (surface) is given to the quantities referring to the pellet surface; the subscript b (bulk), to the quantities referring to the flow core. The external-diffusion problem is more general, since boundary conditions (10) are a particular case of expressions (11) and (12) at $K_{mi} \rightarrow \infty$ and $K_T \rightarrow \infty$.

For any rate r_i of the complex HCR (route rate or rate for some component), it is possible to introduce the

concept of surface and bulk efficiency factors. These factors are the ratios of a given rate in the pellet to the same rates on the pellet surface and in the flow core, respectively, at fixed concentrations and temperature:

$$\eta_{is} = \frac{\int r_i dV}{r_i(\mathbf{C}_s)V_c}, \quad \eta_{ib} = \frac{\int r_i dV}{r_i(\mathbf{C}_b)V_c}. \quad (13)$$

In Eq. (13), V_c is the pellet volume. Note that, for the i th component, the observed reaction rate, which is given by Eq. (1) for the i th reactant, is equal to

$$r_i^{\text{obs}}(\mathbf{P}, T, \mathbf{k}) = r_i(\mathbf{C}_b, T, \mathbf{k})\eta_{ib}q. \quad (14)$$

Here, q is the coefficient converting the reaction rate per unit volume of the pellet, $r_i(\mathbf{C}_b, T)$, to the rate per unit volume of the bed, r_i^{obs} .

It is sufficient to know the factors η_{is} and η_{ib} only for the key components, since these factors for the other components can be calculated using stoichiometric relationships. For example, if $r_3 = r_1 - r_2$, then $\eta_{3s} = (r_1\eta_{1s} - r_2\eta_{2s})/(r_1 - r_2)$ and $\eta_{3b} = (r_1\eta_{1b} - r_2\eta_{2b})/(r_1 - r_2)$. Note also that, for the same reasons, the efficiency factors for complex HCRs can take both positive and negative values.

Using Eq. (7), it can be demonstrated that the efficiency factors for the external-diffusion problem are equal to

$$\begin{aligned} \eta_{is} &= \frac{3K_{mi}(C_{is} - C_{ib})}{ar_i(\mathbf{C}_s)}, \\ \eta_{ib} &= \frac{3K_{mi}(C_{is} - C_{ib})}{ar_i(\mathbf{C}_b)}, \end{aligned} \quad (15)$$

where a is the pellet radius.

Thus, ODE set (1) has to be solved in each step of the minimization of the objective function S for determining the kinetic parameters. In order to calculate the right-hand sides of this set of equations according to Eq. (14), it is necessary to determine the efficiency factors by solving the set of equations (7) and (8) subject to the corresponding boundary conditions followed by integration over the pellet radius (for the internal-diffusion problem) or to calculate these efficiency factors using Eq. (15) (for the external-diffusion problem).

The optimization problems will be solved by the Davidon-Fletcher-Powell procedure [9] using the penalty method [10] to take into account the constraints. The Cauchy problem applied to the ODE sets will be solved by the Gear method for integration of stiff sets of ODEs [11, 12]. Thus, the only challenge is to develop efficient methods for solving equations of multicomponent heat and mass transfer (Eqs. (7) and (8)).

DIFFUSION STOICHIOMETRY RELATIONSHIPS

In order to establish diffusion stoichiometry relationships in a general form, we will use the familiar relationships between different rates of the complex HCR. The formation rates of the reaction participants (vector \mathbf{r}) are related to the route rates (vector \mathbf{R}) by the matrix of the stoichiometric coefficients of the overall route equations (\mathbf{G}):

$$\mathbf{r} = \mathbf{G}^T \mathbf{R}. \quad (16)$$

The rank of the matrix \mathbf{G} is equal to the number of key components (N_k); that is, it is equal to the number of linearly independent overall route equations. For the sake of simplicity, we will assume that the first N_k columns of the matrix \mathbf{G}^T (matrix \mathbf{G}_1) are linearly independent. In this case, Eq. (16) will appear as

$$\mathbf{r} = \mathbf{G}_1 \mathbf{R}_1, \quad (17)$$

where \mathbf{R}_1 is the rate vector for the chosen stoichiometric basis of routes. Since the number of key components is N_k , it is always possible to choose a nonsingular square submatrix \mathbf{G}_{11} of size N_k in the matrix \mathbf{G}_1 . For the sake of simplicity, we will assume that the first N_k rows of \mathbf{G}_1 are a nonsingular matrix; then, $\mathbf{G}_1^T = (\mathbf{G}_{11}^T, \mathbf{G}_{12}^T)$.

From Eq. (17), we obtain

$$\mathbf{R}_1 = \mathbf{G}_{11}^{-1} \mathbf{r}_k. \quad (18)$$

In Eq. (18) and hereafter, the subscript k stands for the key components and the subscript d stands for the dependent components. By substituting Eq. (18) into Eq. (17), we obtain the following matrix relationship between the formation rates of dependent and independent reactants for the complex HCR:

$$\mathbf{r}_d = \mathbf{G}_{12} \mathbf{G}_{11}^{-1} \mathbf{r}_k. \quad (19)$$

The integration of Eq. (5) taking into account Eq. (19) yields the following relationship between the flows of the dependent and key reactants:

$$\mathbf{J}_d = \mathbf{G}_{12} \mathbf{G}_{11}^{-1} \mathbf{J}_k. \quad (20)$$

The integration of Eq. (3) taking into account Eq. (20) yields the following general diffusion stoichiometry relationships in matrix form:

$$(\mathbf{C}_d - \mathbf{C}_{ds}) = \mathbf{D}_d^{*-1} \mathbf{G}_{12} \mathbf{G}_{11}^{-1} \mathbf{D}_k^* (\mathbf{C}_k - \mathbf{C}_{ks}), \quad (21)$$

where \mathbf{D}^* is the diagonal matrix of effective diffusion coefficients. In the derivation of Eq. (21), we assumed that the effective diffusion coefficients are constant throughout the pellet. Although Eq. (21) involves the matrices \mathbf{G}_{12} and \mathbf{G}_{11} , which refer to a particular chosen stoichiometric basis of routes, it can be demonstrated that the matrix $\mathbf{G}_{12} \mathbf{G}_{11}^{-1}$ is independent of the route basis

chosen. That is, the linearity coefficients in Eq. (21) are invariant with respect to the choice of the route basis.

Now we will set up a relationship similar to Eq. (21) but referring to temperature rather than the component concentrations. It can readily be demonstrated that

$$\sum_{j=1}^{N_r} (-\Delta H_j) R_j \text{ is independent of the route basis chosen.}$$

Let us introduce the following designations: $-\Delta \mathbf{H}$ is the column vector of heats for the overall equations representing the initial routes and $-\Delta \mathbf{H}_1$ is the column vector of heats for the overall equations corresponding to the chosen stoichiometric basis of routes. Using only the heats and rates of the nonempty routes of the stoichiometric basis of routes, we obtain

$$\begin{aligned} \sum_{j=1}^{N_r} (-\Delta H_j) R_j &= -\Delta \mathbf{H}^T \mathbf{R} \\ &= -\Delta \mathbf{H}_1^T \mathbf{R}_1 = (-\Delta \mathbf{H}_1^T) \mathbf{G}_{11}^{-1} \mathbf{r}_k. \end{aligned}$$

Using Eq. (6), we obtain

$$\text{div } \mathbf{J}_T = (-\Delta \mathbf{H}_1^T) \mathbf{G}_{11}^{-1} \text{div } \mathbf{J}_k. \quad (22)$$

Integrating Eq. (22) and taking into account the zero boundary conditions at the pellet center, we arrive at

$$\mathbf{J}_T = (-\Delta \mathbf{H}_1^T) \mathbf{G}_{11}^{-1} \mathbf{J}_k. \quad (23)$$

Substituting the flux from Eq. (23) into Eq. (4) and integrating the resulting equation with respect to r , we obtain the following relationship between the temperature at any point of the pellet and the key component concentrations:

$$T - T_s = (-\Delta \mathbf{H}_1^T) \mathbf{G}_{11}^{-1} \mathbf{D}_k^* (\mathbf{C}_k - \mathbf{C}_{ks}) / \lambda^*. \quad (24)$$

Thus, relationships (21) and (24) enable one to calculate the concentrations and temperatures of all substances inside the pellet provided that the concentrations and temperatures of all substances on the pellet surface and the concentrations of the key components in the pellet bulk are known.

In order to develop an efficient difference scheme, let us relate the concentrations of the dependent reactants and the surface temperature to the concentrations of all components and temperature in the flow core and the key component concentrations on the pellet surface.

Relationships (20) and (23) are valid throughout the pellet, including its surface. From these relationships subject to the pellet-surface boundary conditions (11) and (12), we derive the following linear relationships:

$$(\mathbf{C}_{ds} - \mathbf{C}_{db}) = (\mathbf{K}_{md})^{-1} \mathbf{G}_{12} \mathbf{G}_{11}^{-1} \mathbf{K}_{mk} (\mathbf{C}_{ks} - \mathbf{C}_{kb}), \quad (25)$$

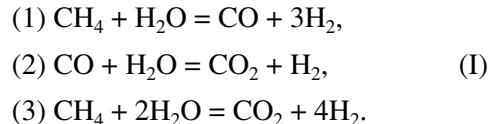
$$T_s - T_b = (-\Delta \mathbf{H}_1^T) \mathbf{G}_{11}^{-1} \mathbf{K}_{mk} (\mathbf{C}_{ks} - \mathbf{C}_{kb}) / K_T. \quad (26)$$

In the derivation of Eq. (25), as distinct from Eqs. (21) and (24), we made no assumptions as to the constancy of effective diffusion coefficients in the pellet.

Relationships (21) and (24) provide an opportunity to solve only Eq. (7) for the key components instead of solving the complete set of equations (Eqs. (7) and (8)), which consists of $N_t + 1$ equations for component concentrations and temperature in the pellet, since they allow the concentrations of the other components and the temperature to be calculated.

Note that the general diffusion stoichiometry relationships were also set up in other works [8, 14]. The difference between our approach and the approach reported by Christiansen and Jarvan [8] is that our relationships are applicable to any HCR, no matter what the reaction mechanism and the form of the overall equations. As distinct from the relationships suggested by Pisarenko and Pisarenko [14], our relationships follow directly from Fick's and Fourier's laws and are, therefore, much easier to derive. Relationships (21), (23), and (24) provided a basis for the finite-difference algorithm presented below and for a computer program using this algorithm to calculate the external and internal heat and mass transfer for the catalyst pellet. This program is part of a program for solving inverse kinetic problems involving diffusion limitations.

The above will be illustrated by the example of steam methane reforming on a nickel catalyst. We will rely on the mechanism and route equations accepted by Xu and Froment [15]:



Let the reactants be numbered as follows: methane, 1; carbon dioxide, 2; hydrogen, 3; water vapor, 4; carbon monoxide, 5. The number of key components in this reaction is two. Xu and Froment [15] chose the key components to be CH_4 ($i = 1$) and CO_2 ($i = 2$). The stoichiometric matrix for the overall equations appears as

$$\mathbf{G} = \begin{pmatrix} -1 & 0 & 3 & -1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ -1 & 1 & 4 & -2 & 0 \end{pmatrix}.$$

Let us choose routes 1 and 2 in scheme (I) to be the nonempty routes of the stoichiometric basis. The following matrices will then be obtained:

$$\mathbf{G}_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \\ 3 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}, \quad \mathbf{G}_{11} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\mathbf{G}_{11}^{-1} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathbf{G}_{12} = \begin{pmatrix} 3 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix},$$

$$\mathbf{G}_{12}\mathbf{G}_{11}^{-1} = \begin{pmatrix} -3 & 1 \\ 1 & -1 \\ -1 & -1 \end{pmatrix}.$$

The diffusion stoichiometry relationships will appear as

$$(C_3 - C_{3s}) = -\frac{3D_1^*}{D_3^*}(C_1 - C_{1s}) + \frac{D_2^*}{D_3^*}(C_2 - C_{2s}),$$

$$(C_4 - C_{4s}) = \frac{D_1^*}{D_4^*}(C_1 - C_{1s}) - \frac{D_2^*}{D_4^*}(C_2 - C_{2s}),$$

$$(C_5 - C_{5s}) = -\frac{D_1^*}{D_5^*}(C_1 - C_{1s}) - \frac{D_2^*}{D_5^*}(C_2 - C_{2s}).$$

The expression for temperature appears as

$$T = T_s + [\Delta H_1 D_1^*(C_1 - C_{1s}) - \Delta H_2 D_2^*(C_2 - C_{2s})]/\lambda^*,$$

where $-\Delta H_1$ and $-\Delta H_2$ are the heats of reactions 1 and 2 in scheme (I). Relationship (25), (26) will take the form

$$(C_{3s} - C_{3b}) = -\frac{3K_{m1}}{K_{m3}}(C_{1s} - C_{1b}) + \frac{K_{m2}}{K_{m3}}(C_{2s} - C_{2b}),$$

$$(C_{4s} - C_{4b}) = \frac{K_{m1}}{K_{m4}}(C_{1s} - C_{1b}) - \frac{K_{m2}}{K_{m4}}(C_{2s} - C_{2b}),$$

$$(C_{5s} - C_{5b}) = -\frac{K_{m1}}{K_{m5}}(C_{1s} - C_{1b}) - \frac{K_{m2}}{K_{m5}}(C_{2s} - C_{2b}),$$

$$T_s = T_b + [\Delta H_1 K_{m1}(C_{1s} - C_{1b}) - \Delta H_2 K_{m2}(C_{2s} - C_{2b})]/K_T.$$

Note that, in the general case, inert substances may be present in the reaction mixture. Their concentrations do not appear in the above formulas, but they must be taken into consideration in the calculation effective diffusion coefficients and mass and heat transfer coefficients.

COMPUTATIONAL METHOD FOR THE HEAT AND MASS TRANSFER EQUATIONS

This section details our numerical method of solving the equations of heat and mass transfer on the catalyst pellet [16]. In order to numerically solve Eq. (3) as applied to the key components, we will turn to the unsteady-state problem and introduce the dimensionless pellet radius $\rho = r/a$. The set of equations (3) for the key components is

$$\frac{\partial C_l}{\partial t} = \frac{\partial^2 C_l}{\partial \rho^2} + \frac{2\partial C_l}{\rho \partial \rho} + \frac{a^2}{D_l^*} r_l = 0, \quad 0 \leq \rho \leq 1, \quad l = 1, \dots, N_k \quad (27)$$

subject to the boundary conditions

$$\begin{aligned} -\frac{\partial C_l}{\partial \rho}(1) &= \frac{aK_{ml}}{D_l^*}(C_{ls} - C_{lb}), \\ \frac{\partial C_l}{\partial \rho}(0) &= 0, \quad k = 1, \dots, N_k. \end{aligned} \quad (28)$$

Problem (27), (28) should be solved with respect to time until the establishment of the steady state that is the solution of the set of equations (3). The initial concentrations along the pellet radius will be taken to be equal to the constant concentrations in the flow core:

$$C_l(\rho, 0) = C_{lb}, \quad l = 1, \dots, N_k. \quad (29)$$

The mixed problem (27)–(29) will be solved using a difference scheme similar to that suggested by Slin'ko et al. [17] for solving the internal-diffusion problem for a one-component system:

$$\begin{aligned} \frac{(C_l)_n^{f+1} - (C_l)_n^f}{\tau} &= \frac{(C_l)_{n+1}^{f+1} - 2(C_l)_n^{f+1} + (C_l)_{n-1}^{f+1}}{h^2} \\ &+ \frac{2}{(n-0.5)h} \frac{(C_l)_{n+1}^{f+1} - (C_l)_{n-1}^{f+1}}{2h} + \frac{(r_l)_n^f}{D_l^*} a^2, \\ n &= 1, \dots, N-1, \quad f = 0, \dots, \\ l &= 1, \dots, N_k, \\ h &= 1/(N-0.5). \end{aligned} \quad (30)$$

In Eq. (30), N is the number of points in the difference scheme, f is the number of the time layer, and h is the step size of the difference scheme. The equality of the flows to zero at the pellet center is expressed as

$$(C_l)_0^f = (C_l)_1^f. \quad (31)$$

The following difference boundary conditions will be accepted for the problem of external diffusion on the pellet surface:

$$\begin{aligned} \frac{(C_l)_N - (C_l)_N}{h} &= \frac{aK_{ml}}{D_l^*}(C_{lN} - C_{lb}), \\ l &= 1, \dots, N_k. \end{aligned} \quad (32)$$

For the internal-diffusion problem, the boundary conditions on the pellet surface appear as

$$(C_l)_N = C_{ls} \quad l = 1, \dots, N_k. \quad (33)$$

The set of difference equations (30)–(33) defines an implicit difference scheme, which can be solved by the sweep method [18]. We will consider the computational procedure for the external-diffusion problem, which is more general and more complicated than the internal-

diffusion problem. For the zero time layer, we will take $C_{ls} = C_{lb}$ and $T_s = T_b$. The reaction rate in the $(f+1)$ th layer is derived from the concentrations and temperature in the f th layer. After the key component concentrations in the $(f+1)$ th layer are calculated by the sweep method, the concentrations of the dependent reactants and the pellet surface temperature are determined using relationships (25) and (26). The values thus calculated will be used in the next time layer to calculate the dependent reactant concentrations and the pellet bulk temperature using diffusion stoichiometry relationship (21) and temperature equation (24). The computational procedure is terminated once the efficiency factors of the key components have become time-invariable.

It is essential to calculate the physicochemical parameters of the model, namely, the effective diffusion coefficients and the mass and heat transfer coefficients. The effective diffusion coefficients (which have dimensions of cm^2/s in the above formulas) are calculated using the following procedure:

(1) The binary diffusion coefficients are determined using, e.g., the Fuller–Schletter–Giddings formula [19]:

$$D_{AB} = \frac{10^{-3} T^{1.75} [1/M_A + 1/M_B]^{0.5}}{P [(\sum v)_A^{1/3} + (\sum v)_B^{1/3}]^2},$$

where M_A and M_B are the molecular weights of the components A and B, P is pressure (atm), and $(\sum v)_A$ and $(\sum v)_B$ are the atomic diffusion volumes.

(2) The molecular diffusion coefficient of the i th component is calculated using the following formula [2]:

$$D_{mi} = (1 - x_i) / \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}},$$

where x_i is the mole fraction of the i th component.

(3) The Knudsen diffusion coefficients are determined using the following formula [2]:

$$D_{Ki} = 4850 \delta \sqrt{T/M_i},$$

where δ is the diameter of a straight cylindrical pore (cm) and M_i is the molecular weight of the i th component.

(4) The diffusion coefficient for the pores of radius r is calculated:

$$\frac{1}{D_{i,r}} = \frac{1}{D_{mi}} + \frac{1}{D_{Ki}}.$$

(5) The average diffusion coefficient in the pores is calculated taking into account the volumetric pore-size distribution [20]:

$$D_i = \sum_r D_{i,r} \frac{\Delta V_r}{V_t},$$

where ΔV_r is the volume of the pores with a given radius and V_t is the total pore volume.

(6) Finally, the Knudsen diffusion coefficient is determined as

$$D_i^* = \frac{\epsilon}{\tau} D_i,$$

where ϵ is porosity and τ is the tortuosity of the pellet (ϵ/τ is diffusion permeability).

The mass transfer coefficient K_{mi} and the heat transfer coefficient K_T are calculated using familiar correlations [21]. The viscosity, heat conductivity, and heat capacity of gas mixtures (and, if necessary, more precise values of binary diffusion coefficients) can be calculated using our program for calculating the physicochemical properties of gas mixtures (including non-ideal ones). This program is based on formulas and recommendations suggested by Reid et al. [19].

EXAMPLE CALCULATION

In order to illustrate the above computational procedure, we will consider experimental data for methane steam reforming over a Ni catalyst under nearly industrial conditions [22] and the results of processing these data [15].

The experiments [22] were carried out in an isothermal flow reactor at 773, 798, 823, and 848 K in the pressure range of 3 to 15 bar. The H_2/CH_4 ratio at the reactor inlet was maintained at 1.25; the $\text{H}_2\text{O}/\text{CH}_4$ ratio, at 3 or 5. The catalyst consisted of 0.18–0.25 or 0.3–0.4 mm granules. In all runs, the catalyst weight was 0.4 g. At each temperature, six kinetic curves were recorded as the dependence of the methane conversion x_{CH_4} and the product yields x_{CO_2} and x_{CO} on the conditional contact time defined as the ratio of the catalyst weight to the methane feed rate. The conditional contact time was varied by a factor of 5–6. The different activities of different weights of the catalyst were leveled out by applying corrections to the conditional contact time. Most of the results thus obtained are believed to refer to the kinetic regime of the reaction [15, 22].

The outlet concentrations of CO_2 and CO were determined chromatographically, and the flows of these components were calculated. The methane concentration and conversion were derived from the difference between the inlet methane flux and the outlet CO and CO_2 flows.

Xu and Froment [15] suggested a three-route mechanism consisting of the overall route equations (I). In this mechanism, each route rate is limited by one step that is different from the rate-limiting steps of the other routes. The other steps of the mechanism are consid-

Table 1. Kinetic parameters of steam methane reforming according to mechanism (I)

Variant	$\ln A_1$	E_1/R	$\ln A_2$	E_2/R_3	$\ln A_3$	E_3/R	$\ln A_{\text{CO}}$	E_{CO}/R	$\ln A_{\text{H}_2}$	E_{H_2}/R	$\ln A_{\text{CH}_4}$	E_{CH_4}/R	$\ln A_{\text{H}_2\text{O}}$	$E_{\text{H}_2\text{O}}/R$
1	36.0	-28.9	14.5	-8.08	34.6	-29.4	-9.91	8.50	-18.9	9.98	-7.32	4.61	12.1	-10.7
2	37.5	-29.9	12.4	-6.58	42.8	-33.5	-8.01	7.87	-20.0	7.04	-5.00	4.09	11.5	-9.00
3	37.2	-30.1	13.2	-5.38	42.9	-33.9	-8.12	7.72	-19.5	7.33	-5.26	3.90	11.0	-8.99

ered to be equilibrium. The route rate equations are written as follows [15]:

$$R_1 = \frac{k_1}{P_{\text{H}_2}^{2.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_1} \right) / (\text{DEN})^2,$$

$$R_2 = \frac{k_2}{P_{\text{H}_2}} \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_2} \right) / (\text{DEN})^2, \quad (34)$$

$$R_3 = \frac{k_3}{P_{\text{H}_2}^{3.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}}^3 - \frac{P_{\text{H}_2}^4 P_{\text{CO}_2}}{K_3} \right) / (\text{DEN})^2,$$

where $\text{DEN} = 1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2}$.

These reaction rates considered in [15] have dimensions of $\text{mol g}_{\text{Cat}}^{-1} \text{h}^{-1}$. For this reason, we will use the following dimensions in Eq. (34): the rate constants of reactions 1 and 3 in scheme (I) (k_1 and k_3), $\text{mol bar}^{1/2} \text{g}_{\text{Cat}}^{-1} \text{h}^{-1}$; the rate constant of reaction 2 (k_2), $\text{mol g}_{\text{Cat}}^{-1} \text{h}^{-1} \text{bar}^{-1}$; the CH_4 , CO , and H_2 adsorption equilibrium constants (K_{CH_4} , K_{CO} , and K_{H_2} , respectively), bar^{-1} ; the equilibrium constant of the dissociative adsorption of water ($\text{H}_2\text{O} + \text{Z} \rightleftharpoons \text{ZO} + \text{H}_2$, $K_{\text{H}_2\text{O}}$), dimensionless; the equilibrium constants of reactions 1 and 3 (K_1 and K_3), bar^2 ; the equilibrium constant of reaction 2 (K_2), dimensionless.

Xu and Froment [15] fitted kinetic parameters by minimizing the sum of squared relative deviations between experimental and calculated x_{CH_4} and x_{CO_2} data for low x_{CO} yields (that is, the kinetic parameters were derived from a single quantity). We found that the yield $x_{\text{CO}} = x_{\text{CH}_4} - x_{\text{CO}_2}$ calculated using the parameters reported by Xu and Froment [15] exceeds the experimental value by a factor of 2–3. Therefore, those parameters [15] do not adequately describe the CO partial pressure as a function of the contact time.

For this reason the kinetic parameters were refitted under the assumption that the experiments were conducted in the kinetic regime. The fitting procedure was based on minimizing the sum of squared relative deviations for x_{CO} and x_{CO_2} . The mean relative error in the

CO_2 and CO yields was 6.76 and 8.94%, respectively. Next, we ran programs implementing the above methods to judge the process controlling the reaction, fit the kinetic parameters to experimental data, and calculate efficiency factors. To do this, we used porosity, the pore radius distribution (mercury porosimetry), and tortuosity data [20]. The latter parameter in [20] was estimated by solving the inverse problem for diffusion-controlled runs under the assumptions that the parameters reported by Xu and Froment [15] are true kinetic parameters. In general, the diffusion permeability of a catalyst should either be measured directly (e.g., by the Wicke–Kallenbach method [21]) or be refined when solving the inverse problem, using experimental data definitely referring to diffusion control.

The parameters taken from [15] (variant 1), the parameters fitted under the assumption that the reaction is kinetically controlled (variant 2), and the parameters fitted without making this assumption (variant 3) are listed in Table 1 ($\ln k_i$ or $\ln K_i = \ln A_i + E_i/R$).

The ranges of variation of the efficiency factors for the kinetic parameters thus determined are listed in Table 2. To illustrate the fact that the efficiency factors for a multiroute reaction can take any value (all the more so for a reverse reaction), we present the methane, carbon dioxide, and carbon monoxide efficiency factors, although it is sufficient to know the efficiency factors for any two components in the case of methane reforming. As is clear from the data presented in Table 2, the model used by Xu and Froment [15, 22] in the calculation of heat and mass transfer on the catalyst pellet suggests that the reaction proceeded in a region where both the internal diffusion factors and mass transfer from the flow core to the surface of the catalyst pellet

Table 2. Methane, carbon dioxide, and carbon monoxide efficiency factors at various temperatures [14, 21]

Efficiency factor	Temperature, K			
	773	798	823	848
$\eta_b(\text{CH}_4)$	0.78–0.84	0.63–0.65	0.61–0.65	0.56–0.60
$\eta_s(\text{CH}_4)$	0.84–0.88	0.72–0.77	0.69–0.78	0.66–0.71
$\eta_b(\text{CO}_2)$	0.76–0.81	0.70–0.75	0.66–0.71	0.53–0.62
$\eta_s(\text{CO}_2)$	0.81–0.84	0.78–0.83	0.73–0.77	0.62–0.69
$\eta_b(\text{CO})$	0.56–5.55	0.59–2.87	0.39–0.96	0.38–0.74
$\eta_s(\text{CO})$	1.59–5.56	0.92–2.78	0.63–1.41	0.64–1.01

are significant. The temperature difference between the flow core and the surface did not exceed 3 K, and the pellet was nearly isothermal. Note that the efficiency factors reported by Xu and Froment [20] for an industrial methane reforming reactor can also take any value.

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