

Mathematical Modeling of the Chemical Reaction Kinetics in the Quasi-equilibrium and Quasi-stationary Approximation

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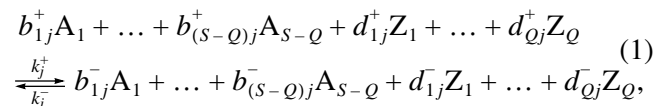
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Abstract—A new, more general algorithm is proposed for modeling reaction kinetics in the quasi-equilibrium and quasi-stationary approximation. This algorithm is substantiated, special cases are considered, and necessary relationships are derived.

When modeling the kinetics of a composite chemical reaction, it is necessary to take into account all available information on the reaction mechanism. Modeling reaction kinetics under the assumption that the fast reversible steps are at quasi-equilibrium and that the concentrations of the highly reactive intermediates are quasi-stationary is detailed in [1–4]. However, only Snagovskii and Ostrovskii [2] proposed a correct method for developing kinetic models in the quasi-equilibrium and quasi-stationary approximation. They considered the problem under some constraints and restricted themselves to special cases.

In this work, we put forward a new, more general algorithm for modeling reaction kinetics in the quasi-equilibrium and quasi-stationary approximation.

Consider a composite chemical reaction including R step and taking place in a system of S reactants. Of these S reactants, let Q reactants be highly reactive intermediates (hereafter, intermediates) and $(S - Q)$ reactants be stable. The stable reactants will be denoted by A_i , $i = 1, 2, \dots, (S - Q)$, and the intermediates will be denoted by Z_u ($u = 1, 2, \dots, Q$). The reaction mechanism will then be described by the following equations:



where $j = 1, 2, \dots, R$.

The law of mass action implies the following expressions for the rates of reaction steps:

$$p_j = k_j^+ \prod_{i=1}^{S-Q} c_i^{b_{ij}^+} \prod_{u=1}^Q z_u^{d_{uj}^+} - k_j^- \prod_{i=1}^{S-Q} c_i^{b_{ij}^-} \prod_{u=1}^Q z_u^{d_{uj}^-}. \quad (2)$$

In Eqs. (1) and (2), b_{ij}^+ and b_{ij}^- are the stoichiometric coefficients of the stable reactants, d_{uj}^+ and d_{uj}^- are the stoichiometric coefficients of the intermediates, c_i are

the concentrations of the stable reactants, and z_u are the concentrations of the intermediates.

If the reaction takes place at a constant temperature and volume, the step rate vector can be divided into two subvectors characterizing the changes time variation of the concentrations of the stable reactants intermediates:

$$\begin{aligned} d\mathbf{c}/dt &= [dc_1/dt, dc_2/dt, \dots, dc_{S-Q}/dt]^T, \\ d\mathbf{z}/dt &= [dz_1/dt, dz_2/dt, \dots, dz_Q/dt]^T. \end{aligned}$$

Likewise, the complete set of kinetic equations,

$$\frac{d}{dt} \begin{bmatrix} \mathbf{c} \\ \mathbf{z} \end{bmatrix} = \mathbf{Bp}[\mathbf{c}, \mathbf{z}, \mathbf{k}], \quad \begin{bmatrix} \mathbf{c}(0) \\ \mathbf{z}(0) \end{bmatrix} = \begin{bmatrix} \mathbf{c}^0 \\ \mathbf{z}^0 \end{bmatrix}$$

can be divided into two subsystems:

$$d\mathbf{c}/dt = \mathbf{B}_y \mathbf{p}, \quad \mathbf{c}(0) = \mathbf{c}^0; \quad (3)$$

$$d\mathbf{z}/dt = \mathbf{B}_a \mathbf{p}, \quad \mathbf{z}(0) = \mathbf{z}^0. \quad (4)$$

Here, \mathbf{B}_y and \mathbf{B}_a are the stoichiometric matrices for the stable reactants and intermediates, respectively.

Suppose that some of the R steps (and, accordingly, some of the columns of the stoichiometric matrix \mathbf{B}) may be linearly dependent: $\text{rk } \mathbf{B} \leq R$. The rank of matrix \mathbf{B}_a is generally lower than the number of rows: $\text{rk } \mathbf{B}_a = I \leq Q$. Let us arrange the I basis rows of matrix \mathbf{B}_a into a submatrix \mathbf{B}_{ab} of size $I \times R$. This submatrix has a full row rank: $\text{rk } \mathbf{B}_{ab} = I$. Furthermore, let us assemble the other rows of matrix \mathbf{B}_a into a submatrix \mathbf{B}_{a3} of size $(Q - I) \times R$. Since \mathbf{B}_{ab} consists of the basis rows of matrix \mathbf{B}_a , the rows of matrix \mathbf{B}_{a3} can be expressed in terms of rows of the matrix \mathbf{B}_{ab} (by analogy with the linear relationship between the concentrations of the key and nonkey reactants [1]):

$$\mathbf{B}_{a3} = \mathbf{G}_{a3}^T \mathbf{B}_{ab}, \quad (5)$$

where \mathbf{G}_{a3}^T is a linear transformation matrix of the form

$$\mathbf{G}_{a3}^T = \mathbf{B}_{a3}\mathbf{B}_{ab}^- = \mathbf{B}_{a3}\mathbf{B}_{ab}^T[\mathbf{B}_{ab}\mathbf{B}_{ab}^T]^{-1}.$$

Let us divide the set of Eqs. (4) into two subsets involving \mathbf{B}_{ab} and \mathbf{B}_{a3} :

$$\begin{aligned} d\mathbf{z}_b/dt &= \mathbf{B}_{ab}\mathbf{p}, \quad \mathbf{z}_b(0) = \mathbf{z}_b^0; \\ d\mathbf{z}_3/dt &= \mathbf{B}_{a3}\mathbf{p}, \quad \mathbf{z}_3(0) = \mathbf{z}_3^0. \end{aligned} \quad (6)$$

Let us premultiply the first equation of set (6) by the linear transformation matrix \mathbf{G}_{a3}^T and subtract the resulting equation from the second equation of set (6). Thereby, we replace the second equation of set (6) with

$$d\mathbf{z}_3/dt - \mathbf{G}_{a3}^T[d\mathbf{z}_b/dt] = \mathbf{B}_{a3}\mathbf{p} - \mathbf{G}_{a3}^T\mathbf{B}_{ab}\mathbf{p}.$$

Since $\mathbf{G}_{a3}^T\mathbf{B}_{ab} = \mathbf{B}_{a3}$,

$$\frac{d}{dt}[\mathbf{z}_3 - \mathbf{G}_{a3}^T\mathbf{z}_b] = \mathbf{0}. \quad (7)$$

Integrating Eq. (7) gives the following relationship between the concentrations of the basis and dependent intermediates:

$$\mathbf{z}_3 - \mathbf{G}_{a3}^T\mathbf{z}_b = \mathbf{z}_3^0 - \mathbf{G}_{a3}^T\mathbf{z}_b^0 = \mathbf{d} = \text{const.} \quad (8)$$

From Eq. (8), knowing the vectors \mathbf{z}_b^0 and \mathbf{z}_3^0 of the initial concentrations of the intermediates and the vector \mathbf{z}_b of the current concentrations of the basis intermediates, we can express the vector \mathbf{z}_3 of the current concentrations of the dependent intermediates:

$$\mathbf{z}_3 = \mathbf{z}_3^0 + \mathbf{G}_{a3}^T[\mathbf{z}_b - \mathbf{z}_b^0]. \quad (9)$$

Suppose that, of the R steps, R_b are fast and reversible and $(R - R_b)$ are slow. Suppose as well that, stoichiometrically, the fast steps are linearly independent.

Under quasi-stationary conditions, the overall formation rate (rate of appearance minus rate of disappearance) of an intermediate is negligible as compared to the rates of the steps or to the reaction rates with respect to stable reactants [5]: $dz_i/dt \ll r_j$ or $dz_j/dt \ll dc_i/dt$. Passing to the limit, we assume that $dz_i/dt \rightarrow 0$.

When writing a set of kinetic equations in the quasi-stationary and quasi-equilibrium approximations, one should take into account the relationships between $\text{rk}\mathbf{B}$, I , and R_b . Apparently, the quasi-stationarity condition for the intermediate concentrations can be met only when the following inequality is valid:

$$I < \text{rk}\mathbf{B}. \quad (10)$$

At the same time, the quasi-equilibrium condition for the fast reversible steps is satisfied if

$$R_b < \text{rk}\mathbf{B}. \quad (11)$$

The quantities I and R_b can be related as $I = R_b$, $I > R_b$, or $I < R_b$. Let us construct a set of kinetic equations for each of these cases.

The number of basis intermediates is equal to the number of independent fast steps. With allowance made for inequality (10), we will compile a set of $\text{rk}\mathbf{B}$ differential equations for the concentrations of $\text{rk}\mathbf{B}$ key reactants. The set of key reactants comprises I basis intermediates and $(\text{rk}\mathbf{B} - I)$ stable reactants, whose concentrations are given by vectors \mathbf{z}_b and \mathbf{c}_{k1} , respectively. The vector composed of these subvectors corresponds to the submatrix \mathbf{B}_k compiled of the respective block matrices:

$$\mathbf{c}_k = \begin{bmatrix} \mathbf{z}_b \\ \mathbf{c}_{k1} \end{bmatrix}, \quad \mathbf{B}_k = \begin{bmatrix} \mathbf{B}_k^b & \mathbf{B}_k^m \end{bmatrix} = \begin{bmatrix} \mathbf{B}_{k1}^b & \mathbf{B}_{k1}^m \\ \mathbf{B}_{k2}^b & \mathbf{B}_{k2}^m \end{bmatrix}. \quad (12)$$

The superscripts b and m stand for fast and slow steps, respectively. Arrays (12) are compiled under the assumption that \mathbf{B}_{k1}^b is nondegenerate.

To partition the vector of the concentrations of the key reactants according to formulas (12), it is necessary that the rows representing basis intermediates appear at the top of submatrix \mathbf{B}_k , followed by the rows representing key stable reactants. Moreover, the columns representing fast steps must go first, followed by the columns representing slow steps. Accordingly, we will partition the vector of kinetic functions into subvectors of the kinetic functions of fast and slow steps:

$$\mathbf{p} = \begin{bmatrix} \mathbf{p}_b \\ \mathbf{p}_m \end{bmatrix}. \quad (13)$$

Taking into account formulas (12) and (13), we obtain the following set of differential equations for the concentrations of the key reactants:

$$\begin{aligned} d\mathbf{z}_b/dt &= \mathbf{B}_{k1}^b\mathbf{p}_b + \mathbf{B}_{k1}^m\mathbf{p}_m, \quad \mathbf{z}_b(0) = \mathbf{z}_b^0; \\ d\mathbf{c}_{k1}/dt &= \mathbf{B}_{k2}^b\mathbf{p}_b + \mathbf{B}_{k2}^m\mathbf{p}_m, \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0. \end{aligned} \quad (14)$$

Let us denote the characteristic rate constants for the fast and slow steps by k_b and k_m , respectively, and let us introduce a small parameter ε and characteristic time λ :

$$\varepsilon = k_m/k_b, \quad \lambda = k_m t.$$

In this notation, set (14) is written as

$$\begin{aligned} \varepsilon \frac{d\mathbf{z}_b}{d\lambda} &= \mathbf{B}_{k1}^b\mathbf{p}_b^* + \varepsilon\mathbf{B}_{k1}^m\mathbf{p}_m^*, \quad \mathbf{z}_b(0) = \mathbf{z}_b^0; \\ \varepsilon \frac{d\mathbf{c}_{k1}}{d\lambda} &= \mathbf{B}_{k2}^b\mathbf{p}_b^* + \varepsilon\mathbf{B}_{k2}^m\mathbf{p}_m^*, \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0, \end{aligned} \quad (15)$$

where $\mathbf{p}_b^* = \mathbf{p}_b/k_b$ and $\mathbf{p}_m^* = \mathbf{p}_m/k_m$.

To obtain a closed set, we are lacking $(S - \text{rk} \mathbf{B} - Q + I)$ equations for the concentrations of the nonkey stable reactants.

Let \mathbf{c}_{nk} be the vector of the concentrations of the nonkey stable reactants and \mathbf{B}_{nk} be the corresponding stoichiometric matrix. Then, the relationship between the vector of the concentrations of the nonkey stable reactants and the vector of the concentrations of the key reactants is given (as above) by the expression

$$\mathbf{c}_{nk} = \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^T [\mathbf{c}_k - \mathbf{c}_k^0] \quad (16)$$

with the linear transformation matrix

$$\mathbf{G}_{nk}^T = \mathbf{B}_{nk} \mathbf{B}_k^{-1} = \mathbf{B}_{nk} \mathbf{B}_k^T [\mathbf{B}_k \mathbf{B}_k^T]^{-1}. \quad (17)$$

The vector \mathbf{c}_k of the concentrations of the key reactants can be partitioned into subvectors of the concentrations of the key intermediates and stable reactants (see Eq. (12)). Let us partition the linear transformation matrix into analogous matrices. Then, Eq. (16) is rewritten as

$$\mathbf{c}_{nk} = \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T1} [\mathbf{z}_b - \mathbf{z}_b^0] + \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0]. \quad (18)$$

If the changes in the concentrations of the basis intermediates are ignored, that is, if it is assumed that

$$\mathbf{z}_b - \mathbf{z}_b^0 = \mathbf{0}, \quad (19)$$

then Eq. (18) can be reduced to

$$\mathbf{c}_{nk} = \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0]. \quad (20)$$

Thus, we have derived a closed set of kinetic equations that includes $\text{rk} \mathbf{B}$ differential equations for the concentrations of the key stable reactants and intermediates, $(Q - I)$ mass balance equations in the concentrations of the intermediate reactants, and $(S - \text{rk} \mathbf{B} - Q + I)$ linear algebraic relationships between the concentrations of the nonkey reactants and the concentrations of the key stable reactants.

To obtain a set of kinetic equations that is suitable for calculations, we transform set (15) under the assumption that the fast reversible steps are at quasi-equilibrium and that the concentrations of the intermediate reactants are quasi-stationary.

First, we will consider the case where the matrix \mathbf{B}_{k2}^b is zero, i.e., the set of stable reactants contains $(\text{rk} \mathbf{B} - R_b)$ key reactants that are not involved in fast steps. In this case, we can pass to the $\varepsilon \rightarrow 0$ limit in the first equation of set (15) and the second equation of set (15) can be rewritten as

$$d\mathbf{c}_{k1}/dt = \mathbf{B}_{k2}^m \mathbf{p}_m [\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}], \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0.$$

Thereby, we obtain the following closed set of kinetic equations:

$$\begin{aligned} \mathbf{p}_b [\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}] &= \mathbf{0}, \\ \mathbf{z}_3 &= \mathbf{z}_3^0 + \mathbf{G}_{a3}^T [\mathbf{z}_b - \mathbf{z}_b^0], \\ \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0], \\ d\mathbf{c}_{k1}/dt &= \mathbf{B}_{k2}^m \mathbf{p}_m [\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}], \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0. \end{aligned} \quad (21)$$

By solving the first two equations of set (21) for the concentrations \mathbf{z}_b and \mathbf{z}_3 of the intermediate reactants and substituting the solutions and the third relation into the last equation, we arrive at a set of differential equations for the concentrations \mathbf{c}_{k1} of the key reactants. Then, knowing the concentrations \mathbf{c}_{k1} as functions of time, we can find the concentrations of the other stable reactants as functions of time.

Now, let us consider the more general case where matrix \mathbf{B}_{k2}^b is nonzero. In this case, we cannot pass to the $\varepsilon \rightarrow 0$ limit in set (15): otherwise, we will lose information and will obtain a nonclosed set of kinetic equations. We can avoid this by transforming the full-column-rank matrix \mathbf{B}_k^b . For this purpose, the vertical matrix \mathbf{B}_k of full column rank must be converted by a nondegenerate linear transformation of rows into a new matrix in which the basis rows (the rows constituting the nondegenerate matrix \mathbf{B}_{k1}^b) are the same and the other rows (the rows constituting matrix \mathbf{B}_{k2}) are zero.

Matrices \mathbf{B}_{k2}^b and \mathbf{B}_{k1}^b are related by the formula

$$\mathbf{B}_{k2}^b = \mathbf{G}_{21}^T \mathbf{B}_{k1}^b. \quad (22)$$

Hence,

$$\mathbf{G}_{21}^T = \mathbf{B}_{k2}^b [\mathbf{B}_{k1}^b]^{-1}.$$

Now, let us premultiply the linear transformation matrix \mathbf{G}_{21}^T by the left- and right-hand sides of the first equation of set (14) and subtract the resulting equation from the second equation of set (14):

$$\begin{aligned} \frac{d\mathbf{c}_{k1}}{dt} - \mathbf{G}_{21}^T \frac{d\mathbf{z}_b}{dt} \\ = \mathbf{B}_{k1}^b \mathbf{p}_b + \mathbf{B}_{k1}^m \mathbf{p}_m - \mathbf{G}_{21}^T \mathbf{B}_{k1}^b \mathbf{p}_b - \mathbf{G}_{21}^T \mathbf{B}_{k1}^m \mathbf{p}_m. \end{aligned} \quad (23)$$

Let us introduce $\mathbf{w} = \mathbf{c}_{k1} - \mathbf{G}_{21}^T \mathbf{z}_b$. Then, in view of formula (22), Eq. (23) is transformed to

$$\begin{aligned} d\mathbf{w}/dt &= [\mathbf{B}_{k2}^m - \mathbf{G}_{21}^T \mathbf{B}_{k1}^m] \mathbf{p}_m, \\ \mathbf{w}(0) &= \mathbf{c}_{k1}^0 - \mathbf{G}_{21}^T \mathbf{z}_b^0 = \mathbf{w}^0. \end{aligned} \quad (24)$$

The dimension of the first equation of set (15) is equal to the dimension of vector \mathbf{p}_b . Since it is assumed above that $\det \mathbf{B}_{k1}^b \neq 0$, we can pass to the $\varepsilon \rightarrow 0$ limit in the first equation of set (15):

$$\mathbf{p}_b [\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}] = \mathbf{0}. \quad (25)$$

Thus, passing to the $\varepsilon \rightarrow 0$ limit in the first equation of set (15) and neglecting the concentrations of the intermediates in Eq. (24) with regard for the linear relationships between the concentrations of the nonkey and key reactants, we arrive at the following closed set of kinetic equations for a reaction that has fast reversible

steps and involves highly active reactants on condition that the number of key active reactants is equal to the number of independent fast reversible steps:

$$\begin{aligned} \mathbf{p}_b[\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}] &= \mathbf{0}, \\ \mathbf{z}_3 &= \mathbf{z}_3^0 + \mathbf{G}_{a3}^T[\mathbf{z}_b - \mathbf{z}_b^0], \\ \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T2}[\mathbf{c}_{k1} - \mathbf{c}_{k1}^0], \\ d\mathbf{c}_{k1}/dt &= [\mathbf{B}_{k2}^m - \mathbf{G}_{21}^T \mathbf{B}_{k1}^m] \mathbf{p}_m[\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}], \\ \mathbf{c}_{k1}(0) &= \mathbf{c}_{k1}^0. \end{aligned} \quad (26)$$

At $\mathbf{B}_{k2}^b = \mathbf{0}$, $\mathbf{G}_{21}^T = \mathbf{0}$ and set (26) reduces to set (21). The last equation of set (26) is derived from Eq. (24) using the expression $d\mathbf{w} \cong d[\mathbf{c}_{k1} - \mathbf{G}_{21}^T \mathbf{z}_b]$.

The number of basis intermediates exceeds the number of fast steps. In this case, the vector \mathbf{c}_k of the concentrations of the key reactants and the corresponding stoichiometric matrix \mathbf{B}_k can be partitioned into blocks:

$$\mathbf{c}_k = \begin{bmatrix} \mathbf{z}_{b1} \\ \mathbf{z}_{b2} \\ \mathbf{c}_{k2} \end{bmatrix}, \quad \mathbf{B}_k = \begin{bmatrix} \mathbf{B}_k^b & \mathbf{B}_k^m \end{bmatrix} = \begin{bmatrix} \mathbf{B}_{k1}^b & \mathbf{B}_{k1}^m \\ \mathbf{B}_{k2}^b & \mathbf{B}_{k2}^m \\ \mathbf{B}_{k3}^b & \mathbf{B}_{k3}^m \end{bmatrix}. \quad (27)$$

According to formulas (27), complete full set of kinetic equations can be represented as

$$\begin{aligned} d\mathbf{z}_{b1}/dt &= \mathbf{B}_{k1}^b \mathbf{p}_b + \mathbf{B}_{k1}^m \mathbf{p}_m, \quad \mathbf{z}_{b1}(0) = \mathbf{z}_{b1}^0; \\ d\mathbf{z}_{b2}/dt &= \mathbf{B}_{k2}^b \mathbf{p}_b + \mathbf{B}_{k2}^m \mathbf{p}_m, \quad \mathbf{z}_{b2}(0) = \mathbf{z}_{b2}^0; \\ d\mathbf{c}_{k2}/dt &= \mathbf{B}_{k3}^b \mathbf{p}_b + \mathbf{B}_{k3}^m \mathbf{p}_m, \quad \mathbf{c}_{k2}(0) = \mathbf{c}_{k2}^0. \end{aligned} \quad (28)$$

In the first equation of set (28), we can introduce a small parameter ε and a characteristic time λ and pass to the $\varepsilon \rightarrow 0$ limit:

$$\varepsilon(d\mathbf{z}_{b1}/dt) = \mathbf{B}_{k1}^b \mathbf{p}_b^* + \varepsilon \mathbf{B}_{k1}^m \mathbf{p}_m^*, \quad \mathbf{z}_{b1}(0) = \mathbf{z}_{b1}^0. \quad (29)$$

Passing to the limit is possible here, because matrix \mathbf{B}_{k1}^b is assumed to be nondegenerate. Therefore, passing to the $\varepsilon \rightarrow 0$ limit allows Eq. (29) to be replaced by the equation

$$\mathbf{p}_{b1}[\mathbf{z}_{b1}, \mathbf{z}_{b2}, \mathbf{c}_{k2}, \mathbf{c}_{nk}] = \mathbf{0}. \quad (30)$$

In the general case where \mathbf{B}_{k2}^b and \mathbf{B}_{k3}^b are nonzero, we cannot pass to the limit in the last two equations of set (28). These equations can be transformed using the expressions relating matrices \mathbf{B}_{k2}^b and \mathbf{B}_{k3}^b to matrix \mathbf{B}_{k1}^b (which are similar to formula (22)):

$$\mathbf{B}_{k2}^b = \mathbf{G}_{21}^T \mathbf{B}_{k1}^b, \quad \mathbf{B}_{k3}^b = \mathbf{G}_{31}^T \mathbf{B}_{k1}^b, \quad (31)$$

where $\mathbf{G}_{21}^T = \mathbf{B}_{k2}^b [\mathbf{B}_{k1}^b]^{-1}$ and $\mathbf{G}_{31}^T = \mathbf{B}_{k3}^b [\mathbf{B}_{k1}^b]^{-1}$.

After transformations similar to transformations defined by formula (22), we obtain

$$\begin{aligned} d\mathbf{w}_z/dt &= [\mathbf{B}_{k2}^m - \mathbf{G}_{21}^T \mathbf{B}_{k1}^m] \mathbf{p}_m, \\ \mathbf{w}_z(0) &= \mathbf{z}_{b2}^0 - \mathbf{G}_{21}^T \mathbf{z}_{b1}^0 = \mathbf{w}_z^0; \\ d\mathbf{w}_c/dt &= [\mathbf{B}_{k3}^m - \mathbf{G}_{31}^T \mathbf{B}_{k1}^m] \mathbf{p}_m, \\ \mathbf{w}_c(0) &= \mathbf{c}_{k2}^0 - \mathbf{G}_{31}^T \mathbf{z}_{b1}^0 = \mathbf{w}_c^0, \end{aligned} \quad (32)$$

where $\mathbf{w}_z = \mathbf{z}_{b2} - \mathbf{G}_{21}^T \mathbf{z}_{b1}$ and $\mathbf{w}_c = \mathbf{c}_{k2} - \mathbf{G}_{31}^T \mathbf{z}_{b1}$.

The vector of the concentrations of the nonkey reactants is expressed in terms of the vector of the concentrations of the key reactants by the following formulas (which are similar to formulas (18) and (19)):

$$\begin{aligned} \mathbf{z}_3 &= \mathbf{z}_3^0 + \mathbf{G}_{a3}^T[\mathbf{z}_b - \mathbf{z}_b^0], \\ \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T1}[\mathbf{z}_{b1} - \mathbf{z}_{b1}^0] \\ &+ \mathbf{G}_{nk}^{T2}[\mathbf{z}_{b2} - \mathbf{z}_{b2}^0] + \mathbf{G}_{nk}^{T3}[\mathbf{c}_{k2} - \mathbf{c}_{k2}^0]. \end{aligned} \quad (33)$$

Combining Eqs. (30), (32), and (33) and neglecting the concentrations of the intermediates (which are low compared to the concentrations of the stable reactants), we arrive at the following closed set of kinetic equations for the case of $I > R_b$:

$$\begin{aligned} \mathbf{p}_b[\mathbf{z}_{b1}, \mathbf{z}_{b2}, \mathbf{z}_3, \mathbf{c}_{k2}, \mathbf{c}_{nk}] &= \mathbf{0}, \\ \mathbf{z}_3 &= \mathbf{z}_3^0 + \mathbf{G}_{a3}^T[\mathbf{z}_b - \mathbf{z}_b^0], \\ [\mathbf{B}_{k2}^m - \mathbf{G}_{21}^T \mathbf{B}_{k1}^m] \mathbf{p}_m[\mathbf{z}_{b1}, \mathbf{z}_{b2}, \mathbf{z}_3, \mathbf{c}_{k2}, \mathbf{c}_{nk}] &= \mathbf{0}, \\ \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T3}[\mathbf{c}_{k2} - \mathbf{c}_{k2}^0], \\ d\mathbf{c}_{k2}/dt &= [\mathbf{B}_{k3}^m - \mathbf{G}_{31}^T \mathbf{B}_{k1}^m] \mathbf{p}_m[\mathbf{z}_{b1}, \mathbf{z}_{b2}, \mathbf{z}_3, \mathbf{c}_{k2}, \mathbf{c}_{nk}], \\ \mathbf{c}_{k2}(0) &= \mathbf{c}_{k2}^0. \end{aligned} \quad (34)$$

The number of fast steps exceeds the number of basis intermediate reactants. In this case, the set of key reactants comprises I basis intermediates and $(\text{rk} \mathbf{B} - I)$ stable reactants and is divided into two subsets. Let us partition vector \mathbf{c}_k and matrix \mathbf{B}_k into blocks:

$$\mathbf{c}_k = \begin{bmatrix} \mathbf{z}_b \\ \mathbf{c}_{k1} \\ \mathbf{c}_{k2} \end{bmatrix}, \quad \mathbf{B}_k = \begin{bmatrix} \mathbf{B}_k^b & \mathbf{B}_k^m \end{bmatrix} = \begin{bmatrix} \mathbf{B}_{k1}^b & \mathbf{B}_{k1}^m \\ \mathbf{B}_{k2}^b & \mathbf{B}_{k2}^m \\ \mathbf{B}_{k3}^b & \mathbf{B}_{k3}^m \end{bmatrix}.$$

This matrix is compiled so that the matrix

$$\mathbf{B}_{k0} = \begin{bmatrix} \mathbf{B}_{k1}^b \\ \mathbf{B}_{k2}^b \end{bmatrix}$$

is nondegenerate:

$$\text{rk} \mathbf{B}_{k0}^b = \text{rk} \mathbf{B}_k^b = R_b, \quad \det \mathbf{B}_{k0}^b \neq 0.$$

The step rate vector is also partitioned into two subvectors:

$$\mathbf{p} = [\mathbf{p}_b \quad \mathbf{p}_m]^T.$$

Then, the set of differential kinetic equations for the concentrations of the key reactants can be written as

$$\begin{aligned} d\mathbf{z}_b/dt &= \mathbf{B}_{k1}^b \mathbf{p}_b + \mathbf{B}_{k1}^m \mathbf{p}_m, \quad \mathbf{z}_b(0) = \mathbf{z}_b^0; \\ d\mathbf{c}_{k1}/dt &= \mathbf{B}_{k2}^b \mathbf{p}_b + \mathbf{B}_{k2}^m \mathbf{p}_m, \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0; \\ d\mathbf{c}_{k2}/dt &= \mathbf{B}_{k3}^b \mathbf{p}_b + \mathbf{B}_{k3}^m \mathbf{p}_m, \quad \mathbf{c}_{k2}(0) = \mathbf{c}_{k2}^0. \end{aligned} \quad (35)$$

Introducing a small parameter ε and reduced time λ , we transform set (35) to

$$\begin{aligned} \varepsilon(d\mathbf{z}_b/d\lambda) &= \mathbf{B}_{k1}^b \mathbf{p}_b^* + \varepsilon \mathbf{B}_{k1}^m \mathbf{p}_m^*, \quad \mathbf{z}_b(0) = \mathbf{z}_b^0; \\ d\mathbf{c}_{k1}/d\lambda &= \mathbf{B}_{k2}^b \mathbf{p}_b + \mathbf{B}_{k2}^m \mathbf{p}_m, \quad \mathbf{c}_{k1}(0) = \mathbf{c}_{k1}^0; \\ d\mathbf{c}_{k2}/d\lambda &= \mathbf{B}_{k3}^b \mathbf{p}_b + \mathbf{B}_{k3}^m \mathbf{p}_m, \quad \mathbf{c}_{k2}(0) = \mathbf{c}_{k2}^0. \end{aligned} \quad (36)$$

The following mass balance equation is valid:

$$\mathbf{z}_3 = \mathbf{z}_3^0 + \mathbf{G}_{a3}^T [\mathbf{z}_b - \mathbf{z}_b^0]. \quad (37)$$

It relates the concentrations of the dependent and independent intermediates. Moreover, by analogy with formula (33), the concentrations of the nonkey stable reactants are related to the concentrations of the key stable reactants by the expression

$$\begin{aligned} \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T1} [\mathbf{z}_{b1} - \mathbf{z}_{b1}^0] \\ &+ \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0] + \mathbf{G}_{nk}^{T3} [\mathbf{c}_{k2} - \mathbf{c}_{k2}^0]. \end{aligned} \quad (38)$$

Neglecting the changes in the concentrations of the intermediates (i.e., taking $\mathbf{z}_{b1} - \mathbf{z}_{b1}^0 \approx 0$), we can rewrite expression (38) as

$$\mathbf{c}_{nk} = \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0] + \mathbf{G}_{nk}^{T3} [\mathbf{c}_{k2} - \mathbf{c}_{k2}^0]. \quad (39)$$

Since matrix \mathbf{B}_{k0}^b is assumed to be nondegenerate, we can write the following relationship between matrices \mathbf{B}_{k3}^b and \mathbf{B}_{k0}^b :

$$\mathbf{B}_{k3}^b = \mathbf{G}_{30}^T \mathbf{B}_{k0}^b, \quad \mathbf{G}_{30}^T = \mathbf{B}_{k3}^b [\mathbf{B}_{k0}^b]^{-1}. \quad (40)$$

Using formula (40), we transform the third equation of set (36) to

$$d\mathbf{c}_{k2}/d\lambda = \mathbf{G}_{30}^T \mathbf{B}_{k0}^b \mathbf{p}_b + \mathbf{B}_{k3}^m \mathbf{p}_m, \quad \mathbf{c}_{k2}(0) = \mathbf{c}_{k2}^0.$$

Let us multiply the left- and right-hand sides of the first two equations of set (35) by the linear transformation

matrices \mathbf{G}_{30}^{T1} and \mathbf{G}_{30}^{T2} obtained by the concordant partitioning of matrix \mathbf{G}_{30}^T according to the formulas

$$\begin{aligned} \mathbf{B}_{k3}^b &= \mathbf{G}_{30}^T \mathbf{B}_{k0}^b \\ &= \begin{bmatrix} \mathbf{G}_{30}^{T1} & \mathbf{G}_{30}^{T2} \end{bmatrix} \begin{bmatrix} \mathbf{B}_{k1}^b \\ \mathbf{B}_{k2}^b \end{bmatrix} = \mathbf{G}_{30}^{T1} \mathbf{B}_{k1}^b + \mathbf{G}_{30}^{T2} \mathbf{B}_{k2}^b. \end{aligned} \quad (41)$$

Add the equations obtained and subtract their sum from the third equation of set (35) to obtain

$$\begin{aligned} \frac{d}{dt} [\mathbf{c}_{k2} - \mathbf{G}_{30}^{T1} \mathbf{z}_{b1} - \mathbf{G}_{30}^{T2} \mathbf{c}_{k1}] \\ = [\mathbf{B}_{k3}^b - \mathbf{G}_{30}^{T1} \mathbf{B}_{k1}^b - \mathbf{G}_{30}^{T2} \mathbf{B}_{k2}^b] \mathbf{p}_b \\ + [\mathbf{B}_{k3}^m - \mathbf{G}_{30}^{T1} \mathbf{B}_{k1}^m - \mathbf{G}_{30}^{T2} \mathbf{B}_{k2}^m] \mathbf{p}_m. \end{aligned} \quad (42)$$

Taking into account Eqs. (35) and (40), we can replace Eq. (42) with

$$\begin{aligned} d\mathbf{w}/dt &= [\mathbf{B}_{k3}^m - \mathbf{G}_{30}^{T1} \mathbf{B}_{k1}^m - \mathbf{G}_{30}^{T2} \mathbf{B}_{k2}^m] \mathbf{p}_m, \\ \mathbf{w}(0) &= \mathbf{w}^0. \end{aligned} \quad (43)$$

It is clear from the left-hand sides of Eqs. (42) and (43) that

$$\mathbf{w} = \mathbf{c}_{k2} - \begin{bmatrix} \mathbf{G}_{30}^{T1} & \mathbf{G}_{30}^{T2} \end{bmatrix} \begin{bmatrix} \mathbf{z}_{b1} \\ \mathbf{c}_{k1} \end{bmatrix} \approx \mathbf{c}_{k2} - \mathbf{G}_{30}^{T2} \mathbf{c}_{k1}. \quad (44)$$

Passing to the $\varepsilon \rightarrow 0$ limit in the first equation of set (36) gives

$$\mathbf{p}[\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{k2}, \mathbf{c}_{nk}] = \mathbf{0}. \quad (45)$$

Thus, the kinetics of the reaction under consideration in the case of $R_b > I$ is described by the following closed set of algebraic and differential equations:

$$\begin{aligned} \mathbf{p}_b[\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{k2}, \mathbf{c}_{nk}] &= \mathbf{0}, \\ \mathbf{z}_3 &= \mathbf{z}_3^0 + \mathbf{G}_{a3}^T [\mathbf{z}_b - \mathbf{z}_b^0], \\ \mathbf{c}_{nk} &= \mathbf{c}_{nk}^0 + \mathbf{G}_{nk}^{T2} [\mathbf{c}_{k1} - \mathbf{c}_{k1}^0] + \mathbf{G}_{nk}^{T3} [\mathbf{c}_{k2} - \mathbf{c}_{k2}^0], \end{aligned} \quad (46)$$

$$\begin{aligned} d\mathbf{w}/dt &= [\mathbf{B}_{k3}^m - \mathbf{G}_{30}^{T1} \mathbf{B}_{k1}^m - \mathbf{G}_{30}^{T2} \mathbf{B}_{k2}^m] \mathbf{p}_m[\mathbf{z}_b, \mathbf{z}_3, \mathbf{c}_{k1}, \mathbf{c}_{nk}], \\ \mathbf{w}(0) &= \mathbf{w}^0. \end{aligned}$$

In all the equations of this set, \mathbf{c}_{k2} must be replaced by the expression

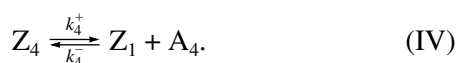
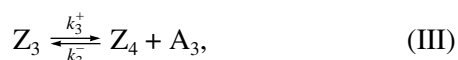
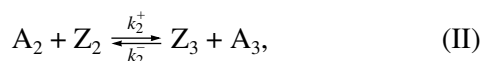
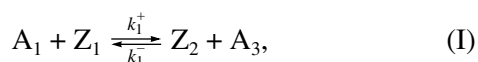
$$\mathbf{c}_{k2} = \mathbf{w} + \mathbf{G}_{30}^{T2} \mathbf{c}_{k1}, \quad (47)$$

which follows from formula (44).

The first equation of set (46) is the condition for the R_b fast steps being at quasi-equilibrium. It must be solved simultaneously for \mathbf{z}_{b1} and \mathbf{c}_{k1} . If matrix \mathbf{B}_{k3}^b (and, accordingly, \mathbf{G}_{30}^T) is zero, then set (46) is simplified.

fied, since $\mathbf{w} = \mathbf{c}_{k2}$. Under these conditions, the reaction kinetics can be described in terms of concentrations without using auxiliary variables. If $I \rightarrow 0$, then the mathematical model (46) is a kinetic model in the quasi-equilibrium approximation.

Let us illustrate our method for constructing a kinetic model in the quasi-equilibrium and quasi-stationary approximation by the example of four-step methane conversion by the linear cyclic mechanism



Here, A_1 — CH_4 , A_2 — H_2O , A_3 — H_2 , A_4 — CO , Z_1 — Z , Z_2 — ZCH_2 , Z_3 — ZCHOH , and Z_4 — ZCO .

This reaction is single-route, and its overall equation is



The third and fourth steps are known to be very fast. The stoichiometric matrix of stable reactants; if compiled so that the first and second columns correspond to the third and fourth steps, will appear as

$$\mathbf{B}_y = \begin{array}{cc|cc} \text{III} & \text{IV} & \text{I} & \text{II} \\ \hline 0 & 0 & -1 & 0 & (c_1) \\ 0 & 0 & 0 & -1 & (c_2) \\ 1 & 0 & 1 & 1 & (c_3) \\ 0 & 1 & 0 & 0 & (c_4) \end{array}. \quad (49)$$

The stoichiometric matrix of the intermediates has the form

$$\mathbf{B}_a = \begin{array}{cc|cc} \text{III} & \text{IV} & \text{I} & \text{II} \\ \hline 0 & 1 & -1 & 0 & (z_1) \\ 0 & 0 & 1 & -1 & (z_2) \\ -1 & 0 & 0 & 1 & (z_3) \\ 1 & -1 & 0 & 0 & (z_4) \end{array}. \quad (50)$$

The step rate vector is written as

$$\mathbf{p} = \begin{bmatrix} \mathbf{p}_b \\ \mathbf{p}_m \end{bmatrix} = \begin{bmatrix} k_3^+ z_3 - k_3^- c_3 z_4 \\ k_4^+ z_4 - k_4^- c_4 z_1 \\ k_1^+ c_1 z_1 - k_1^- c_3 z_2 \\ k_2^+ c_2 z_2 - k_2^- c_3 z_3 \end{bmatrix}. \quad (51)$$

As one can see, $R_b = 2$, $\text{rk} \mathbf{B} = 4$ (the number of linearly independent steps or the rank of the full stoichiometric matrix), and $I = 3$. Consequently, we deal with the case where the number of basis intermediates exceeds the number of fast steps.

Out of the four intermediates ($Q = 4$), we select Z_1 , Z_3 , and Z_2 as basis reactants. The reactant Z_2 is selected because, as is clear from matrix \mathbf{B}_a , it is involved only in slow steps. The reactant A_1 is selected for the same reason: it does not participate in fast steps. Thus, we have the following vector of the concentrations of the key reactants:

$$\mathbf{c}_k = \begin{bmatrix} \mathbf{z}_{b1} \\ \mathbf{z}_{b2} \\ \mathbf{c}_{k2} \end{bmatrix} = \begin{bmatrix} z_1 \\ z_2 \\ z_3 \\ c_1 \end{bmatrix}. \quad (52)$$

The corresponding stoichiometric matrix is

$$\mathbf{B}_k = \begin{bmatrix} \mathbf{B}_k^b & \mathbf{B}_k^m \end{bmatrix} = \begin{bmatrix} \mathbf{B}_{k1}^b & \mathbf{B}_{k1}^m \\ \mathbf{B}_{k2}^b & \mathbf{B}_{k2}^m \\ \mathbf{B}_{k3}^b & \mathbf{B}_{k3}^m \end{bmatrix} = \begin{array}{cc|cc} 0 & 1 & -1 & 0 \\ -1 & 0 & 0 & 1 \\ \hline 0 & 0 & 1 & -1 \\ \hline 0 & 0 & -1 & 0 \end{array}. \quad (53)$$

Since, in this case, we have $\mathbf{B}_{k2}^b = \mathbf{0}$ and $\mathbf{B}_{k3}^b = \mathbf{0}$, the set of algebraic differential equations describing the kinetics of reactions (I)–(IV) has the form

$$\begin{aligned} K_3 z_3 - c_3 z_4 &= 0, \\ K_4 z_4 - c_4 z_1 &= 0, \end{aligned} \quad (54)$$

$$p_1 - p_2 = k_1^+ c_1 z_1 - k_1^- c_3 z_2 - k_2^+ c_2 z_2 + k_2^- c_3 z_3, \quad (55)$$

$$z_1 + z_2 + z_3 + z_4 = 1, \quad (56)$$

$$dc_1/dt = -p_1 = -k_1^+ c_1 z_1 + k_1^- c_3 z_2, \quad c_1(0) = c_1^0, \quad (57)$$

$$c_2 = c_2^0 + c_1 - c_1^0,$$

$$c_3 = c_3^0 - 3(c_1 - c_1^0), \quad (58)$$

$$c_4 = c_4^0 - (c_1 - c_1^0).$$

Equations (54) define quasi-equilibrium conditions for the third and fourth fast steps, and K_3 and K_4 are the respective equilibrium constants. Equation (55) is the quasi-stationarity condition for the concentration of the intermediate Z_2 . Equation (56) is the mass balance equation for this intermediate.

Solving Eqs. (54)–(56) gives an expressions for the concentrations of the intermediates reactant. Substituting these concentrations into Eq. (57) gives an overall kinetic equation. Expressions (58) are consistent with the stoichiometry of the overall reaction.

The stationary rate of this reaction is p_3 . It is equal to the rates of the third and fourth steps (these rates are equal). The expression for p_3 has the form

$$p_3 = \frac{k_1^+ k_2^+ K_3 K_4 c_1 c_2 - k_1^- k_2^- c_3^2 c_4}{\Delta},$$

where

$$\Delta = k_1^+ K_3 K_4 c_1 - k_2^+ K_3 K_4 c_2 + k_1^- K_3 K_4 c_3 + k_2^+ K_3 c_2 c_4 + k_1^- K_3 c_3 c_4 + (k_1^- + k_2^-) c_3^2 c_4 + k_2^+ c_2 c_3 c_4.$$

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