Calculation of rate constants and quantitative description of nonfully defined reaction systems

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A procedure for determining necessary extent of information, completing incomplete data on concentration course of reacting substances and obtaining sufficient basis to calculate the optimum values of rate constants at unambiguous description of nonfully defined reaction system is described in this paper. It is based on the theory of vector spaces applied to mechanisms of chemical reactions and involves construction and analysis of reaction matrix, determination of the dimension of stoichiometric space as well as establishment of a convenient base system of vectors. The proposed procedure of calculation is illustrated by some examples.

Описан метод нахождения необходимой информации для дополнения неполных данных об изменениях в концентрациях реагирующих веществ и для получения достаточных оснований для расчета оптимальных величин констант скоростей при описании не полностью определенной реакционной системы. Метод исходит из приложения теории векторных пространств к изучению механизмов химических реакций и основан на составлении и анализе реакционной матрицы, установлении размера стехиометрического пространства и определении подходящей базисной системы векторов. Предлагаемый метод расчета иллюстрирован на многих примерах.

In the present technical practice, we more and more frequently meet with the problem of quantitative description of nonfully defined complicated reaction systems. As a rule, it is the exigency to calculate definite values of rate constants in a system of differential equations derived on the basis of a supposed or evidenced mechanism valid for a given reaction system while more or less complete data are

available about time course of concentration of the individual components which constitute this reaction system.

In this connection, we must frequently solve the problem concerning the extent of information necessary for a given mechanism to obtain a mathematically unambiguous quantitative description of the whole system from the initial experimental material, *e.g.* by kinetic expression in the form of a system of differential equations with concrete values of rate constants so that it optimally and unambiguously expresses the used initial data.

Theoretical

There are several papers dealing with the problem how to calculate the optimum values of rate constants in complicated kinetic models. Many procedures allowing satisfactorily rapid and reliable calculation were developed in the last two decades [1—19]. All of them require the use of computer and presume the knowledge of time dependence of concentration of all components which are present in the designed kinetic model.

However, the concentration course of all reaction components is not known in general case though these substances take part in the mechanism of the investigated reaction system. For analytical or other reasons, the concentrations of all intermediates, instable complexes, *etc.* are not followed. Then we use the experimental material describing only incompletely the reaction system for our calculation and search for such set of rate constants which optimally expresses this incomplete experimental collection. Different simplifications, *e.g.* application of the known assumption of equilibrium concentration of activated complex, *etc.* are employed. However, there is a question whether the values of rate constants thus obtained also describe the complete experimental data in equally good manner or whether other set of the values of constants describing the complete collection with equal or better fitting does exist. From the mathematical point of view, it is a problem of unambiguousness of solution with respect to the limited starting material. On the other hand, we may so put the question that we inquire about the necessary extent of experimental material guaranteeing unambiguousness of solution, *i.e.* how many components and which of them must be analytically followed in order that the calculated set of rate constants as well as the defined mechanism with corresponding differential equations may give an unambiguous quantitative description of the investigated reaction system.

The first part of this question (determination of the number of stoichiometrically independent components) may be answered by using the application of the mathematics of vector spaces to the problem of mechanisms and kinetics of complicated reactions. The papers recently published in this field were summarized

by *Feinberg* [20]. As our procedure starts from these studies and the cited publication is not currently available, we present the basic description of the analysis, method, and derived theorems.

The reaction system consisting of the m reacting components may be conceived as an m-dimensional vector space IR^M where m unit vectors of the form $e_1 = (1, 0, 0, \quad 0)$, $e_2 = (0, 1, 0, \quad 0)$ up to $e_m = (0, 0, 0, \quad 0, 1)$ exist. If we impose to this reaction system a mechanism consisting of k equations, we may construct k reaction vectors by combining unit vectors and corresponding equations of the used mechanism. These k vectors constitute the so-called reaction matrix $k \times m$. Starting from the initial composition of reaction mixture expressed by a certain point in the m-dimensional space of components, this composition changes with time and forms the so-called composition or reaction trajectory.

A simple example, to a certain extent taken from [20], makes it easier to clear up the preceding description and construction of reaction matrix.

We apply the mechanism

$$(A)$$
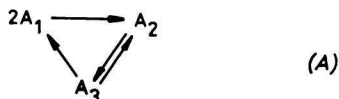
to the three-dimensional space of the components A_1, A_2, and A_3 with unit vectors $e_1 = (1, 0, 0)$, $e_2 = (0, 1, 0)$, and $e_3 = (0, 0, 1)$.

We represent the reaction vector for reaction $2A_1 \rightarrow A_2$ as $e_2 - 2e_1$, for reaction $A_2 \rightarrow A_3$ as $e_3 - e_2$, for inverse reaction $A_3 \rightarrow A_2$ as $e_2 - e_3$, and for reaction $A_3 \rightarrow 2A_1$ as $2e_1 - e_3$. Then we use these vector differences for the construction of the reaction matrix in the form

$$M \quad \begin{bmatrix} -2 & 1 & 0 \\ 0 & -1 & 1 \\ 0 & 1 & -1 \\ 2 & 0 & -1 \end{bmatrix} \quad (1)$$

The number of rows in matrix **M** is the total number of reactions of a given mechanism while the number of columns expresses the number of the components which take part in the mechanism.

Some important conclusions result from the theorems derived in paper [20]. For a fixed mechanism, the reaction trajectory cannot arbitrarily wander in the vector space of components, but it is strictly limited to the so-called stoichiometric subspace S or a space which is parallel with it. The dimension of the stoichiometric space is given by the rank h of the reaction matrix **M**. This subspace expresses the stoichiometric limitations imposed on the general space by the applied mechanism

and all reaction trajectories, irrespective of concrete values of rate constants, must lie in this stoichiometric space or a space which is parallel with it. Since the reaction matrix is frequently singular and its rank is for many mechanisms lower than the number of rows or columns, it appears sometimes that the dimension of the space in which the reaction trajectory can occur is considerably reduced.

As for the concrete example of mechanism (A), the rank of matrix (1) is equal to two and the stoichiometric subspace is formed by a plane in the three-dimensional space of concentrations of the reaction components. If we express the initial composition of reaction mixture by the point (C_1^0, C_2^0, C_3^0), all stoichiometrically compatible compositions of reaction mixture lie on a plane which is parallel with the stoichiometric plane and contains the point (C_1^0, C_2^0, C_3^0). Different composition trajectories appear on this plane at different values of the rate constants and describe the time course of the composition of reaction mixture.

The exposition given by *Feinberg* is rather extensive and for this reason, we refer to original paper [20].

Calculation of the composition of reaction mixture
from incomplete input information

As evident from the preceding text, the application of the above procedure to arbitrary mechanism enables us to determine the dimension of stoichiometric subspace, *i.e.* the number of the components which form a stoichiometrically independent system in a given reaction system. However, it does not answer the second equally important question, *i.e.* which concrete components constitute this independent system and how it is possible to calculate the concentration course of other components regarded as dependent in this connection. In order to solve this problem, we had to develop the above method. We elaborated a procedure which enables us to calculate unambiguously the composition of reaction mixture as a function of time even if the information about time dependence of the concentrations of all participating components is not available and the experimental material is considerably limited in some cases. At the same time, the procedure makes possible to find out which concentration courses must be investigated for determining fully and unambiguously the quantitative relations in reaction system. Its essence is based on these steps:

— construction of a kinetic model which expresses the supposed mechanism,

— formal integration of the model and formation of a system of linear equations,

— construction of a reaction matrix and determination of its rank h,

— calculation of concrete submatrices of the dimension $h \times h$ with nonzero determinant and mutual comparison of these submatrices,

— selection of a convenient and admissible system of independent components,

— expression of balance relations between independent and dependent concentration courses of components.

The dimension of the stoichiometric space given by the rank of reaction matrix **M** determines the number of independent row (reaction) vectors which form the base of the stoichiometric subspace. However, it also gives the number of independent column vectors, *i.e.* the number of the components the concentration courses of which also form the base of the stoichiometric subspace with respect to the pertinent mechanism. The rank of matrix **M** expresses the dimension of the greatest square matrix **M** with nonzero determinant, *i.e.* with columns and rows formed by linearly independent vectors. For instance, if the rank of matrix (*1*) for mechanism (*A*) is equal to two, there are two independent equations in this system and two independent concentrations of components A_i, while two rows and one column of the matrix are a linear combination of other rows and columns (*e.g.* column $1 = -2$ (column $2 +$ column 3), row $3 = -$ row 2, *etc.*).

Of course, the concrete rows and columns representing the base of the stoichiometric subspace cannot be taken arbitrarily even if we know their number (it is given by the rank of reaction matrix) because we could take the vectors which are linearly dependent.

However, by calculating the determinants of all possible square submatrices of the dimensions $h \times h$ we find out which of them are constituted as a system of linearly independent row and column vectors (determinant different from zero).

Their number is dependent on the mechanism used. The serial numbers of columns in these matrices give those components the concentrations of which are linearly independent for a given mechanism and thus form one of possible bases of the stoichiometric space. Among various possibilities we choose that one which is the most convenient from the experimental and analytical point of view. Then other column or row vectors are a linear combination of base vectors.

In the calculation we proceed as follows:

1. On the basis of the chosen or fixed mechanism we construct a system of m differential equations, one equation for each reaction component. Respecting the validity of the law of mass action, we express the functional dependence of the rate on the composition of mixture for each partial equation of mechanism and in order to simplify the calculation, we solve each reversible reaction as one kinetic unit.

For the above-mentioned example (three components of mechanism (A)) we obtain the following expressions:

Equation $2A_1 \rightarrow A_2$

$$f_1 = k_1 C_1^2 \tag{2}$$

Equation $A_2 \rightleftarrows A_3$

$$f_2 = k_2 C_2 - k_3 C_3 \tag{3}$$

Equation $A_3 \rightarrow 2A_1$

$$f_3 = k_4 C_3 \tag{4}$$

The rate equations for individual components are

$$\frac{dC_1}{dt} = -f_1 + f_3 \tag{5}$$

$$\frac{dC_2}{dt} = f_1 - f_2 \tag{6}$$

$$\frac{dC_3}{dt} = f_2 - f_3 \tag{7}$$

2. After integration of the rate equations (in our case $(5—7)$ in the interval from zero to t, we obtain

$$\Delta C_1 \equiv C_1 - C_1^0 = -\int_0^t f_1 \, dt + \int_0^t f_3 \, dt \tag{8}$$

$$\Delta C_2 \equiv C_2 - C_2^0 = \int_0^t f_1 \, dt - \int_0^t f_2 \, dt \tag{9}$$

$$\Delta C_3 \equiv C_3 - C_3^0 = \int_0^t f_2 \, dt - \int_0^t f_3 \, dt \tag{10}$$

3. If we write

$$I_i = \int_0^t f_i \, dt \tag{11}$$

we obtain a system of linear integral equations which assumes for our case the following form

$$\Delta C_1 = -I_1 + I_3 \tag{12}$$
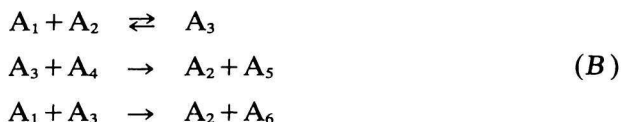
$$\Delta C_2 = I_1 - I_2 \tag{13}$$

$$\Delta C_3 = I_2 - I_3 \tag{14}$$

4. We construct the reaction matrix, determine its rank h and calculate which concrete submatrices of the dimension $h \times h$ have a nonzero determinant. We select a convenient combination of the independently variable columns, *i.e.* concentrations for quantitative description of the system. The concentration courses of other components are to be calculated from the system of linear equations obtained according to passage 3. In our case, it is obvious even from this system of equations that these equations are not independent because it holds

$$\Delta C_1 + \Delta C_2 + \Delta C_3 = 0 \tag{15}$$

654

and provided the concentration course $C_i = f(t)$ is known for two components, the concentration course of the third component can be easily calculated. That is in agreement with the preceding considerations concerning the dimension of stoichiometric subspace S and the rank of matrix (1) which was equal to two. Of course, we need not take into consideration the stoichiometric subspace and reaction matrix for so simple example because the linear dependence of eqns (12—14) is evident. In complicated cases involving a greater number of components and reactions the visual appreciation or casual search for the number and kind of independent variables is not applicable because it does not provide all possibilities of selection.

Let us give two more concrete examples with complete calculation. In a six-component system, the aldol condensation of two aldehydes A_1 and A_4 proceeds in the presence of base A_2 according to the following scheme

$$
\begin{aligned}
A_1 + A_2 &\rightleftarrows A_3 \\
A_3 + A_4 &\rightarrow A_2 + A_5 \\
A_1 + A_3 &\rightarrow A_2 + A_6
\end{aligned}
\qquad (B)
$$

The reaction matrix assumes the form

$$
M_2 \quad
\begin{bmatrix}
-1 & -1 & 1 & 0 & 0 & 0 \\
1 & 1 & -1 & 0 & 0 & 0 \\
0 & 1 & -1 & -1 & 1 & 0 \\
-1 & 1 & -1 & 0 & 0 & 1
\end{bmatrix}
\qquad (16)
$$

and the calculation shows that its rank is $h = 3$.

The concentration courses of components A_1, A_2, and A_4 are available (Table 1,

Table 1

Example of calculation of concentration courses
Aldol condensation of two aldehydes

1	2	3	4	5	6	7
t	C_1	C_2	C_3	C_4	C_5	C_6
min	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}
0	0.083	0.1	0.125	0	0	0
1	0.049	0.050	0.103	0.050	0.022	0.019
2	0.041	0.049	0.089	0.051	0.036	0.022
3	0.032	0.049	0.077	0.051	0.048	0.024
4	0.027	0.049	0.068	0.051	0.057	0.026
6	0.022	0.049	0.054	0.051	0.071	0.030
8	0.019	0.049	0.046	0.051	0.079	0.033

columns *2, 3,* and *4*). Component A_3 is an instable complex and no specific analytical method is known for components A_5 and A_6.

We use the rate functions

$$f_1 = k_1 C_1 C_2 - k_2 C_3 \qquad (17)$$

$$f_2 = k_3 C_3 C_4 \qquad (18)$$

$$f_3 = k_4 C_1 C_3 \qquad (19)$$

for writing the rate equations for individual components

$$\frac{dC_1}{dt} = -f_1 - f_3 \qquad (20)$$

$$\frac{dC_2}{dt} = -f_1 + f_2 + f_3 \qquad (21)$$

$$\frac{dC_3}{dt} = f_1 - f_2 - f_3 \qquad (22)$$

$$\frac{dC_4}{dt} = -f_2 \qquad (23)$$

$$\frac{dC_5}{dt} = f_2 \qquad (24)$$

$$\frac{dC_6}{dt} = f_3 \qquad (25)$$

By integrating these equations, we obtain a system of linear equations in simplified symbolization

$$\Delta C_1 = -I_1 \qquad - I_3 \qquad (26)$$

$$\Delta C_2 = -I_1 + I_2 + I_3 \qquad (27)$$

$$\Delta C_3 = \quad I_1 - I_2 - I_3 \qquad (28)$$

$$\Delta C_4 = \quad - I_2 \qquad (29)$$

$$\Delta C_5 = \quad I_2 \qquad (30)$$

$$\Delta C_6 = \quad I_3 \qquad (31)$$

On the basis of the rank $h = 3$ we calculate the nonzero determinants of all minors 3×3. Their number is twenty-four while the admissible combinations of rows are two (1, 3, 4 and 2, 3, 4). As for the admissible combinations of columns, there are twelve possibilities (*e.g.* 1, 2, 4; 1, 2, 5; 1, 3, 4, *etc.*).

We ascertain that the matrix formed from rows 1, 3, 4 and columns 1, 2, 4 constitutes a linearly independent system. Thus the knowledge of the concentra-

tion courses of components A_1, A_2, and A_4 is sufficient for full description of the reaction system.

We may use eqns (26—31) or immediately the matrix $\mathbf{M_2}$ for deriving the stoichiometric relations for other components
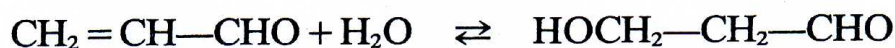
$$\Delta C_3 \equiv C_3 - C_3^0 = -\Delta C_2 \tag{32}$$
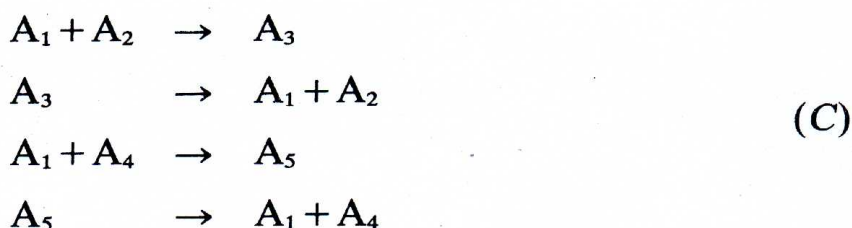
$$\Delta C_5 \equiv C_5 - C_5^0 = -\Delta C_4 \tag{33}$$

$$\Delta C_6 \equiv C_6 - C_6^0 = 1/2(-\Delta C_1 + \Delta C_2 + \Delta C_4) \tag{34}$$

On the basis of these equations and the known values $C_3^0 = C_5^0 = C_6^0 = 0$, we may calculate the corresponding values of concentrations of components A_3, A_5, and A_6 as they are given in Table 1, columns 5, 6, and 7.

The reaction of acrolein with monopentaerythritol in an aqueous weak alkaline medium may be described by the following scheme [21]

$$CH_2 = CH—CHO + H_2O \rightleftarrows HOCH_2—CH_2—CHO$$

$$CH_2 = CH—CHO + C(CH_2OH)_4 \rightleftarrows (CH_2OH)_3C—CH_2OCH_2CH_2CHO$$

which comprises five components and four reactions according to the equations

$$
\begin{array}{rcl}
A_1 + A_2 & \rightarrow & A_3 \\
A_3 & \rightarrow & A_1 + A_2 \\
A_1 + A_4 & \rightarrow & A_5 \\
A_5 & \rightarrow & A_1 + A_4
\end{array}
\tag{C}
$$

The meaning of symbols is:

A_1 — acrolein
A_2 — water
A_3 — 2-hydroxypropanal
A_4 — monopentaerythritol
A_5 — product of the reaction of acrolein with monopentaerythritol

Acrolein and monopentaerythritol are the components which are traced analytically. A typical time course of their concentrations is in Table 2 [21], columns 2 and 3. The concentration course of hydracrolein and product is not known while the relatively small change in water content was not taken into account. The reaction matrix for this system

$$
\mathbf{M_3} =
\begin{bmatrix}
-1 & -1 & 1 & 0 & 0 \\
1 & 1 & -1 & 0 & 0 \\
-1 & 0 & 0 & -1 & 1 \\
1 & 0 & 0 & 1 & -1
\end{bmatrix}
\tag{35}
$$

Table 2

Example of calculation of concentration courses
Reaction of acrolein with monopentaerythritol

1	2	3	4	5
	Known values		Calculated values	
$\dfrac{t}{s}$	$\dfrac{C_1}{\text{mol dm}^{-3}}$	$\dfrac{C_4}{\text{mol dm}^{-3}}$	$\dfrac{C_3}{\text{mol dm}^{-3}}$	$\dfrac{C_5}{\text{mol dm}^{-3}}$
0	9.53×10^{-3}	0.1000	0.0	0.0
200	8.40×10^{-3}	0.0996	0.73×10^{-3}	0.4×10^{-3}
400	7.42×10^{-3}	0.0992	1.31×10^{-3}	0.8×10^{-3}
600	6.57×10^{-3}	0.0989	1.86×10^{-3}	1.1×10^{-3}
800	5.85×10^{-3}	0.0986	2.28×10^{-3}	1.4×10^{-3}
1000	5.23×10^{-3}	0.0984	2.70×10^{-3}	1.6×10^{-3}
1200	4.72×10^{-3}	0.0982	3.01×10^{-3}	1.8×10^{-3}
1400	4.29×10^{-3}	0.0981	3.34×10^{-3}	1.9×10^{-3}
1600	3.95×10^{-3}	0.0980	3.58×10^{-3}	2.0×10^{-3}

has the dimension 4×5, but its rank is only $h = 2$. On integration of the system of rate equations

$$\frac{dC_1}{dt} = -f_1 + f_2 - f_3 + f_4 \tag{36}$$

$$\frac{dC_2}{dt} = -f_1 + f_2 \tag{37}$$

$$\frac{dC_3}{dt} = f_1 - f_2 \tag{38}$$

$$\frac{dC_4}{dt} = -f_3 + f_4 \tag{39}$$

$$\frac{dC_5}{dt} = f_3 - f_4 \tag{40}$$

where

$$f_1 = k_1 C_1 C_2 \tag{41}$$

$$f_2 = k_2 C_3 \tag{42}$$

$$f_3 = k_3 C_1 C_4 \tag{43}$$

$$f_4 = k_4 C_5 \tag{44}$$

we obtain in simplified form

658

$$\Delta C_1 = -I_1 + I_2 - I_3 + I_4 \tag{45}$$

$$\Delta C_2 = -I_1 + I_2 \tag{46}$$

$$\Delta C_3 = I_1 - I_2 \tag{47}$$

$$\Delta C_4 = -I_3 + I_4 \tag{48}$$

$$\Delta C_5 = I_3 - I_4 \tag{49}$$

The nonzero determinants of the minors of matrix M_3 whith the dimension 2×2 enable us to select from eight independent column combinations among which the combination (1, 4) also occurs. Thus we may take components A_1 and A_4 as independent variables and obtain the balance relations from eqns (45—49) which allow us to calculate the concentration course for components A_3 and A_5 (at $C_3^0 = C_5^0 = 0$).

$$C_3 = \Delta C_4 - \Delta C_1 \tag{50}$$

$$C_5 = -\Delta C_4 \tag{51}$$

We could also calculate the change in water concentration according to the equation

$$\Delta C_2 = \Delta C_1 - \Delta C_4 \tag{52}$$

but the concentration of water may be regarded as constant with negligible error provided the reaction takes place in dilute solution.

The calculated values for A_3 and A_5 are given in Table 2, columns 4 and 5. On the basis of these data we may easily calculate the optimum values of rate constants by the procedure described next.

The stoichiometric calculation of the concentration courses for the components with missing data is frequently accompanied by the fact that the errors of experimental values of concentrations of independent components may accumulate in resulting values. That was especially observed if the linear combination of vectors was represented by a more complicated expression or the resulting value of concentration was small when compared with the values of independent components A_i. The calculated concentration course was then not smooth, it was disorderly and necessitated to be smoothed either visually or by regression.

Calculation of the rate constants

For the calculation of rate constants from the known concentration courses of individual reactants on the basis of a given or fixed mathematical model, the method according to *Himmelblau* [3] or in more complicated cases the nonlinear optimization [15—19] proved to be good. We chose the sum of squared differences

(absolute or relative) between the calculated values of concentration of individual components in certain moments of time and the experimental values as a criterion of fit. In order to evaluate the fit, we compared solely the values of those components which formed the base of stoichiometric space because these ones directly determine the concentration courses of other components as well. An evaluation of superfluous number of reactants would not improve the accuracy of result but only complicate the calculation. The determination of the rank of reaction matrix, determinants of the corresponding submatrices with the statement of permitted combinations of linearly independent vectors and the calculation of the optimum system of rate constants nearly always requires the use of a computer. The pertinent programs are partly available and partly have been designed by us.

Symbols

A_i reaction components
C_i concentrations of reaction components
e_i unit vectors in reaction space
f_i rate function
I_i integral of rate function
h rank of reaction matrix
k number of equations of mechanism and number of reaction vectors
k_j rate constant for the j-th equation of mechanism
m number of components of mechanism and dimension of reaction space

Indices

i denotation of the corresponding component; $i = 1, 2, \ldots m$

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