

Matrix and convolution methods in chemical kinetics

Lionello Pogliani

Dipartimento di Chimica, Università della Calabria, 87030 Rende (CS), Italy

Mário N. Berberan-Santos and José M.G. Martinho

Centro de Química-Física Molecular, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

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Two new approaches for writing kinetic equations in the matrix form or directly in the integrated form are presented here. While the first method allows to derive the kinetic rate matrix of kinetic systems of any kind in a direct and straightforward way, the second approach applies to species that are consumed solely through first order steps, regardless of the complexity of their formation pathways.

1. Introduction

The evaluation of the kinetic rate constants and order of a given reaction scheme is usually done by fitting the experimental results with the integrated kinetic equation. For this reason, an important part of the literature on chemical kinetics is focused on the integration of the corresponding rate laws, which are differential equations [1–4]. Normally, this topic consists in studying the fate of a specific reagent or product for several specific cases, that is, first-order, first-order opposing or reversible and consecutive, second-order, second-order reversible, etc. This “state of the art” gives the impression of a lack of unity and leaves the feeling that each case is somewhat unique.

The use of matrices in chemistry and chemical engineering allows the formulation of chemical models in an elegant and compact way. Nevertheless, the integration of kinetic rate equations is frequently presented without recourse to matrix algebra. The matrix formulation of the rate equations (a set of interconnected differential equations, one for the concentration time variation of each species) is particularly convenient since it allows the integration of the rate equations, using a uniform set of procedures. In addition, the time evolution of the concentrations of all species (reagents, products and intermediates) is obtained simultaneously. This topic is only briefly treated in basic texts on chemical kinetics and mathematics for chemistry [5–7], and has been recently reconsidered and further developed by different authors [8–11]. This fact does not limit the definition of a set of rules that can help with the formulation of the rate matrix \mathbf{K} in a direct way. Furthermore,

numerical methods based on the same matrix approach can be used to solve the general case of kinetic systems composed by steps of any order. Analogous formalisms, based on matrices, find many other applications in chemistry and chemical engineering, namely in quantum chemistry (secular equation), spectroscopy (molecular vibrations) and chemical graph theory.

The second part of the paper is devoted to the convolution approach that allows to write kinetic equations directly in the integrated form. However, this approach is limited to kinetic schemes composed of first-order or pseudo first-order elementary steps [12–18]. The method has been recently used for the analysis of complex photochemical kinetic systems [13,17].

2. The matrix method

The first order \mathbf{K} matrix

The construction of a first-order rate matrix \mathbf{K} starts by considering three species (but it can easily be generalized to any number of species) A , B and C that take part in a first- or pseudo first-order chemical kinetic process that can be described by the following 3×3 square matrix (this matrix is normally the transpose of a mathematical matrix):

$$\begin{bmatrix} -k_{AA} & k_{BA} & k_{CA} \\ k_{AB} & -k_{BB} & k_{CB} \\ k_{AC} & k_{BC} & -k_{CC} \end{bmatrix} = \mathbf{K}, \quad (1)$$

where the minus sign along the main diagonal means that along that path species undergo chemical consumption, while k_{II} terms are the rate constants for reactions, $\leftarrow I \rightarrow$, that is, for reactions departing from reactant I and k_{ij} cross-terms are the reaction rate constants of the process $I \rightarrow J$. Thus, while k_{AB} and k_{BA} are the rate constants of $A \rightarrow B$ and $B \rightarrow A$ reactions respectively, k_{AA} is the sum of the rate constants of $A \rightarrow B$ and $A \rightarrow C$ reactions. These \mathbf{K} matrices have two properties [9] (replacing k_{ij} with the corresponding k_i and k_{-i} terms) that help to check their validity: (i) the sum of terms along a column is always zero as the term on the main diagonal is the negative sum of the terms along the respective column and (ii) for reversible reactions the terms on the symmetric sides of the main diagonal differ from each other in their direction (normally indicated by i and $-i$ or f , forward and r , reverse). The rate equation can, thus, be written in the following succinct way (where $d\mathbf{C}/dt = \mathbf{C}'$):

$$\mathbf{C}' = \mathbf{K}\mathbf{C}. \quad (2)$$

Let us now apply the given rules to construct the \mathbf{K} matrices for some reaction schemes.

Consecutive first-order reactions: $A \rightarrow B \rightarrow C$

Here we have $k_{AA} = k_{AB} = k_1$ and $k_{BB} = k_{BC} = k_2$ and the remnants $k_{ii} = 0$, the \mathbf{K} matrix will, then, be

$$\begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} = \mathbf{K}. \quad (3)$$

We notice that while rule 1 is obeyed, rule 2 fails, as the reaction is not reversible.

Opposing first-order consecutive reactions: $A \xrightleftharpoons[k_1]{k_{-1}} B \xrightleftharpoons[k_2]{k_{-2}} C \xrightleftharpoons[k_3]{k_{-3}} D$

Here, $k_{AA} = k_{AB} = k_1$, $k_{BA} = k_{-1}$, $k_{BB} = (k_{-1} + k_2)$, $k_{BC} = k_2$, $k_{CB} = k_{-2}$, $k_{CC} = (k_{-2} + k_3)$, $k_{CD} = k_3$, $k_{DC} = k_{DD} = k_{-3}$, while the restant $k_{ii} = 0$. As there are four species, the rate matrix is a 4×4 matrix:

$$\begin{bmatrix} -k_1 & k_{-1} & 0 & 0 \\ k_1 & -(k_{-1} + k_2) & k_{-2} & 0 \\ 0 & k_2 & -(k_{-2} + k_3) & k_{-3} \\ 0 & 0 & k_3 & -k_{-3} \end{bmatrix} = \mathbf{K}. \quad (4)$$

It is easily seen that, here, rules 1 and 2 are fully respected.

Solution of a first-order consecutive reaction scheme

Kinetic systems composed by unimolecular steps only, the first-order matrices of which do not exceed a 3×3 dimension, are amenable to a rather easy closed form solution by the aid of the matrix eigenvalue method [5,10,11]. Let us take the case of the two-step consecutive scheme (see the preceding paragraph) and the corresponding \mathbf{K} rate matrix. The $\mathbf{C}' = \mathbf{K}\mathbf{C}$ matrix equation, where $\mathbf{C} = (A', B', C')$ and $\mathbf{C} = (A, B, C)$, has the following general solution:

$$\mathbf{C} = \begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix} \cdot \exp(\lambda t) \quad (5)$$

with $\mathbf{C}' = \lambda\mathbf{C}$. By the aid of this solution, eq. (2) leads us to the following matrix eigenvalue problem:

$$\lambda\mathbf{C} = \mathbf{K}\mathbf{C}, \quad (6)$$

since $\lambda\mathbf{C} = \lambda\mathbf{I}\mathbf{C}$, where \mathbf{I} is a unit matrix:

$$(\mathbf{K} - \lambda \mathbf{I})\mathbf{C} = 0. \quad (7)$$

For non-trivial solutions to this equation to exist, the determinant $D = |\mathbf{K} - \lambda \mathbf{I}|$ must be zero. The solution for $D = 0$ yields the eigenvalues $\lambda_1 = 0$, $\lambda_2 = -k_1$ and $\lambda_3 = -k_2$.

The C_1 , C_2 and C_3 eigenvectors belonging to these eigenvalues are calculated from

$$\begin{bmatrix} -(k_1 - \lambda) & 0 & 0 \\ k_1 & -(k_2 - \lambda) & 0 \\ 0 & k_2 & -\lambda \end{bmatrix} \begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix} = 0 \quad (8)$$

and have the following form ($\Delta k = k_2 - k_1$ and L , M and N are three non-zero constants):

$$C_1 = \begin{bmatrix} 0 \\ 0 \\ L \end{bmatrix}, \quad C_2 = \begin{bmatrix} M \\ Mk_1/\Delta k \\ -Mk_2/\Delta k \end{bmatrix} \cdot \exp(-k_1 t), \quad C_3 = \begin{bmatrix} 0 \\ N \\ -N \end{bmatrix} \cdot \exp(-k_2 t). \quad (9)$$

The general solution of the consecutive reaction scheme involving only irreversible first-order steps is then the following linear combination of the three independent eigenvectors C_1 , C_2 and C_3 :

$$C = \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} M \exp(-k_1 t) \\ Mk_1 \exp(-k_1 t)/\Delta k + N \exp(-k_2 t) \\ L \quad -Mk_2 \exp(-k_1 t)/\Delta k - N \exp(-k_2 t) \end{bmatrix}. \quad (10)$$

With the aid of the initial conditions, $C_A(0) = A_0$, $C_B(0) = B_0$ and $C_C(0) = C_0$ and with $S = A_0 + B_0 + C_0$, we obtain

$$A = A_0 \exp(-k_1 t), \quad (10a)$$

$$B = \frac{k_1 A_0}{\Delta k} \{ \exp(-k_1 t) + [B_0 \Delta k - A_0 k_1] \exp(-k_2 t) \}, \quad (10b)$$

$$C = S - \frac{1}{\Delta k} \{ A_0 k_2 \exp(-k_1 t) - [B_0 \Delta k - A_0 k_1] \exp(-k_2 t) \}, \quad (10c)$$

where for $t \rightarrow \infty$ we obtain, as expected, $A = B = 0$ and $C_C = S$.

The second-order K matrix

Rules for the construction of first-order rate matrices can be applied, with small

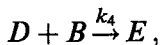
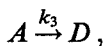
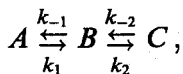
modifications, to construct pure second-order rate matrices with two reactants (A and B) and two products (C and D). Modifications are due to the introduction of the $(C_k)^{n-1}$ concentration term (where $n = 2$) that multiplies with the k_{IJ} rate constant:

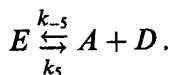
$$\begin{bmatrix} -k_{AA}C_B & k_{BA}C_A & k_{CA}C_D & k_{DA}C_C \\ k_{AB}C_B & -k_{BB}C_A & k_{CB}C_D & k_{DB}C_C \\ k_{AC}C_B & k_{BC}C_A & -k_{CC}C_D & k_{DC}C_C \\ k_{AD}C_B & k_{BD}C_A & k_{CD}C_D & -k_{DD}C_C \end{bmatrix} = \mathbf{K}. \quad (11)$$

The subscript k of the concentration term shows an inverted internal order, that is, $k = B, A, D, C$ relatively to the concentration vector $\mathbf{C} = (C_A, C_B, C_C, C_D)$. This matrix can be converted into a first order rate matrix noticing that for $n = 1$: $(C)^{n-1} = 1$, $C_C = C_D = 0$ and $k_{iC} = k_{iD} = 0$. The given matrix can be simplified in two steps: (1) as there is no internal reaction between reactants or products (that is, A and C do not result from B and D , respectively, and vice versa) we have $k_{AB} = k_{BA} = k_{CD} = k_{DC} = 0$; consequently, (2) as the third and fourth terms in the first and second rows as well as the first and second term in the third and fourth rows are redundant, one of them can be eliminated. These redundancies can be easily detected by simply looking for terms in a row [9] (excluding the terms in the main diagonal) that differ from each other by an internal exchange of reactants or products (namely, by an internal exchange of subscripts). The resulting matrix will then have the following form:

$$\begin{bmatrix} -k_{AA}C_B & 0 & 0 & k_{DA}C_C \\ 0 & -k_{BB}C_A & k_{CB}C_D & 0 \\ 0 & k_{BC}C_A & -k_{CC}C_D & 0 \\ k_{AD}C_B & 0 & 0 & -k_{DD}C_C \end{bmatrix} = \mathbf{K}. \quad (12)$$

Here, the elimination of redundancies has been done in order to obtain a matrix that obeys rules 1 and 2 as well as that "looks nice". With the given method to construct 2nd and, consequently, 1st order matrices it is now possible to construct rate matrices of complex kinetic mechanisms composed of 1st and 2nd order reaction steps, such as





After elimination of redundancies (last row: first $k_{-5}C_D$ term and k_4C_B in the fourth term) we obtain the following rate matrix [9, 11]:

$$\begin{bmatrix} -(k_1 + k_3 + k_{-5}C_D) & k_{-1} & 0 & 0 & k_5 \\ k_1 & -(k_{-1} + k_2 + k_4C_D) & k_{-2} & 0 & 0 \\ 0 & k_2 & -k_{-2} & 0 & 0 \\ k_3 & 0 & 0 & -(k_4C_B + k_{-5}C_A) & k_5 \\ 0 & k_4C_D & 0 & k_{-5}C_A & -k_5 \end{bmatrix} = \mathbf{K}. \quad (13)$$

Clearly, such mixed order matrices do not obey rules 1 and 2.

The concentration vector here is $\mathbf{C} = (C_A, C_B, C_C, C_D, C_E)$. The solution of this kinetic problem is rather formidable and approximations (such as the steady-state or pre-equilibrium approximations) or, even better, numerical methods (such as Euler's or Runge-Kutta's method) have to be invoked to find a solution of the kinetic problem [11, and references therein]. Euler's method, valid also for the time dependent $\mathbf{K}(t)$ (with $k = k(t)$) matrices, solves the matrix equation

$$\mathbf{C}' = \mathbf{K}(t)\mathbf{C}, \quad (14)$$

approximating $\mathbf{C}' = d\mathbf{C}/dt$ by $\Delta\mathbf{C}/\Delta t$

$$\Delta\mathbf{C}/\Delta t = [\mathbf{C}(t + \Delta t) - \mathbf{C}(t)]/\Delta t = \mathbf{K}(t)\mathbf{C}(t); \quad (15)$$

hence (\mathbf{U} being the unit matrix of order n),

$$\mathbf{C}(t + \Delta t) = [\mathbf{U} + \mathbf{K}(t)\Delta t]\mathbf{C}(t). \quad (16)$$

Repeated applications of eq. (16) (with constant or variable time increment Δt), assuming $\mathbf{C}(0)$ to be known, allows the calculation of the concentration of every species at any instant.

In the Runge-Kutta method, which offers a better accuracy, the step is subdivided and $\mathbf{K}(t)$ is computed at selected points in each subinterval. An approximate formula is used to calculate $\mathbf{C}(t)$ for each step. For a differential equation of the form $dy/dx = f(x, y)$ the Runge-Kutta method of the fourth order gives

$$y(x + \Delta x) = y(x) + \Delta x/6(c_1 + 2c_2 + 2c_3 + c_4) \quad (17)$$

with $c_1 = f(x, y)$, $c_2 = f(x + \Delta x/2, y + c_1/2)$, $c_3 = f(x + \Delta x/2, y + c_2/2)$, $c_4 = f(x + \Delta x, y + c_3)$. The method can be extended to solve matrix equation (14), giving in a compact form

$$\mathbf{C}(t + \Delta t) = \mathbf{D}(t)\mathbf{C}(t), \quad (18)$$

where $\mathbf{D}(t)$ is a sum of matrices

$$\mathbf{D}(t) = \mathbf{U} + \Delta t/6[\mathbf{K}(t) + 2\mathbf{K}_1(t)\mathbf{P}(t) + 2\mathbf{K}_2(t)\mathbf{Q}(t) + \mathbf{K}_3(t)\mathbf{R}(t)] \quad (19)$$

with

$$\begin{aligned} \mathbf{P}(t) &= \mathbf{U} + \mathbf{K}(t) \Delta t/2, & \mathbf{Q}(t) &= \mathbf{U} + \mathbf{K}_1(t)\mathbf{P}(t) \Delta t/2, \\ \mathbf{R}(t) &= \mathbf{U} + \mathbf{K}_2(t)\mathbf{Q}(t) \Delta t. \end{aligned} \quad (20)$$

The \mathbf{K}_i are the \mathbf{K} matrices evaluated at different points of the interval, namely,

$$\mathbf{K}_1(t) = \mathbf{K}(\mathbf{P}(t)\mathbf{C}(t)), \quad \mathbf{K}_2(t) = \mathbf{K}(\mathbf{Q}(t)\mathbf{C}(t)), \quad \mathbf{K}_3 = \mathbf{K}(\mathbf{R}(t)\mathbf{C}(t)). \quad (21)$$

Knowing matrix $\mathbf{K}(t)$ and the interval Δt , the $\mathbf{D}(t)$ matrix can be evaluated using eqs. (20) and (21). Once $\mathbf{D}(t)$ is known at a given instant t the value of $\mathbf{C}(t + \Delta t)$ is calculated with the aid of eq. (18). Successive applications of this equation allow the calculation of the time dependence of the concentration of all species.

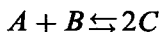
Construction of other types of rate matrices

The second-order matrix (11) can be used as a starting point for the construction of other types of matrices such as matrices of second-order steps with stoichiometric coefficients $\nu_i \neq 1$ or matrices of autocatalytic steps and, clearly, the corresponding matrices of mixed reaction steps.

If in matrix (12) we substitute subscripts D with C , we obtain

$$\begin{bmatrix} -k_{AA}C_B & 0 & 0 & k_{CA}C_C \\ 0 & -k_{BB}C_A & k_{CB}C_C & 0 \\ 0 & k_{BC}C_A & -k_{CC}C_C & 0 \\ k_{AC}C_B & 0 & 0 & -k_{CC}C_C \end{bmatrix} = \mathbf{K}. \quad (22)$$

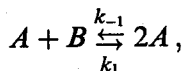
Now, (i) adding the fourth column to the third one and eliminating it, (ii) adding the fourth row to the third one and eliminating it, and (iii) eliminating, successively, the redundant term in the third row (there is a redundancy between the first and second terms of this row), we obtain the rate matrix of the following elementary step with stoichiometric coefficient $\nu_C = 2$:



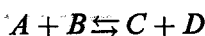
$$\begin{bmatrix} -k_{AA}C_B & 0 & k_{CA}C_C \\ 0 & -k_{BB}C_A & k_{CB}C_C \\ k_{AC}C_B & 0 & -2k_{CC}C_C \end{bmatrix} = \mathbf{K}. \quad (23)$$

Thus, one way to construct rate matrices of reaction steps with nonunitary stoichiometric is: (1) to expand, by the aid of dummy species, the dimension space of the reaction into a space where no equal species are present and (2) to reduce it back to the normal dimension of the reaction operating on the columns and rows of the dummy species. This process, introduced to handle matrices of autocatalytic reaction steps [8], strongly reminds one of the simplex method for solving linear programming problems.

The construction of a rate matrix of the autocatalytic step (k_1 : forward direction, k_{-1} : reverse direction),



starts with matrix (12) where k_{ij} of the dummy reaction scheme



have been substituted by the corresponding k_1 and k_{-1} to prevent errors during the handling of the matrix

$$\begin{bmatrix} -k_1 C_B & 0 & 0 & k_{-1} C_C \\ 0 & -k_1 C_A & k_{-1} C_D & 0 \\ 0 & k_1 C_A & -k_{-1} C_D & 0 \\ k_1 C_B & 0 & 0 & -k_{-1} C_C \end{bmatrix} = \mathbf{K}. \quad (24)$$

Now, by (i) replacing the subscripts C and D by subscript A , (ii) adding the third and fourth columns to the first column and eliminating it, (iii) adding the resulting third and fourth rows to the first row and eliminating it, we obtain

$$\begin{bmatrix} -k_{-1} C_A & k_1 C_A \\ k_{-1} C_A & -k_1 C_A \end{bmatrix} = \mathbf{K}, \quad (27)$$

that is, the rate matrix (with no redundant terms) of the given autocatalytic step that obeys rules 1 and 2. The concentration vector associated with this matrix is $\mathbf{C} = (C_A, C_B)$.

The considered processes that allow to start with a general 2nd order \mathbf{K} matrix and derive specific \mathbf{K} matrices of the same or lower order can be applied to an n th order \mathbf{K} matrix to derive any matrices of lower order, rendering, thus, the method quite general. The same matrix formalism, with minor changes, can also be applied to derive kinetic \mathbf{K} matrices in open systems (in continuous flow stirred tank reactor: CSTR) [9]. In this case two new terms have to be added in each term of the main diagonal: $\Phi \Delta$ and $D_I \nabla^2$, where Φ is the flow rate, Δ is the subtracting operator, that is, $\Delta A = A_0 - A$ (A_0 being the concentration of the input flow), D_I is the diffusion coefficient of species I and ∇^2 is the laplacian operator.

3. The convolution method

Macroscopic chemical kinetics is based on differential equations of the type

$$dC_i/dt = \sum_{k=\text{in,out,pro,con}} (dC_i/dt)_k, \quad (28)$$

which are simple balances for the amount of species C_i ($i = A, B, \dots$) within the system. The sum runs over the four main processes occurring in a chemical reaction: *in* standing for input, *out* for output, *pro* for internal production and *con* for internal consumption; the first two processes are relevant for open systems and the last two are associated with the chemical reactions occurring in the system.

Comparison with experimental data is usually done in the integrated form, that is, the system of differential equations (28) is integrated, analytically or numerically, and the resulting time functions $C_i(t)$ then compared with the experimental ones, in order to extract rate constants or even to test the proposed mechanism/kinetic scheme.

The opposite procedure is also possible, i.e., numerical differentiation of experimental data followed by direct comparison with the system of differential equations (28) (e.g., method of the initial rates). For a number of reasons, which include the amplification of the experimental error, this is a much less common procedure. A general discussion of the advantages and limitations of the differential and integral methods is given by Laidler [2]. More recently, Steel and Razi Naqvi [15] studied the differential method in great detail.

The integration of system (28) can be done using several mathematical techniques, including matrix methods [8–13 and this review]. However, when all the consumption rates (i.e. the *out* and *con* terms in eq. (28)) are of first order (or pseudo-first order) there is a straightforward but little known way to write down the balances directly in the *integrated* form. The method, based on the concept of convolution, is being increasingly used in photochemical kinetics [13 and references therein].

Suppose that a reactive chemical species C_i can be instantaneously produced at unit concentration at time $t = 0$: ignoring the possibility of reformation of C_i via closed loops (e.g. a reversible step), its time evolution will be given by a certain function $C_{i\delta}(t)$. This function is the response to a unit input of C_i at time zero, that is, to a Dirac's delta function $\delta(t)$, and reflects all possible disappearance routes for C_i (Fig. 1). It is, in general, a function of the concentration of C_i and of the concentration of the other species C_j ($j \neq i$). However, *under first-order or pseudo first-order conditions*, this function is independent of all concentrations,

$$C_{i\delta}(t) = \exp\left(-\sum_j k_{ij}t\right), \quad (29)$$

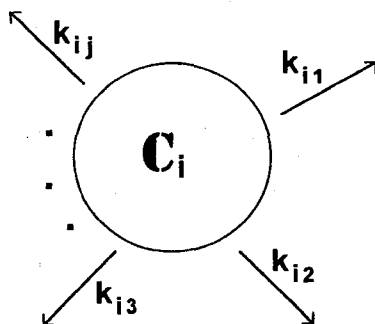


Fig. 1. The possible disappearance routes for C_i .

where k_{ij} are strict first- or pseudo first-order rate constants of the elementary steps by which C_i disappears. Now the general time evolution for C_i is given by the convolution integral

$$C_i(t) = \int_0^t P_i(\theta) C_{i\delta}(t - \theta) d\theta = P_i \otimes C_{i\delta}, \quad (30)$$

where $P_i(t)$ is the rate of production of C_i . This production rate includes all steps that generate C_i , either internal or external, and arising or not from closed loops. Eq. (30) is the fundamental equation of the convolution approach and can be understood on the basis of Fig. 2. The total concentration of C_i at a given instant t will be the sum of all delta responses $C_{i\delta}$ weighted by the respective initial amount produced, $P_i(\theta)$, and taking into account that a time lapse $t - \theta$ has passed since that particular creation process.

Taking the time derivative of eq. (30) yields [13], of course, the usual differential balance

$$dC_i/dt = P_i - \left(\sum_j k_{ij} \right) C_i, \quad (31)$$

this being the proof of the equivalence of the differential and convolution (integral) approaches.

For a given kinetic problem, the full solution in terms of the convolution approach is obtained in four steps:

- (1) identification of the delta responses $C_{i\delta}(t)$;
- (2) identification of the production terms $P_i(t)$;
- (3) writing of the system of coupled (through the P_i 's) integral equations $C_i = P_i \otimes C_{i\delta}$ ($i = A, B, \dots$);
- (4) solution of the system of coupled equations, e.g. by the use of Laplace transformation theory.

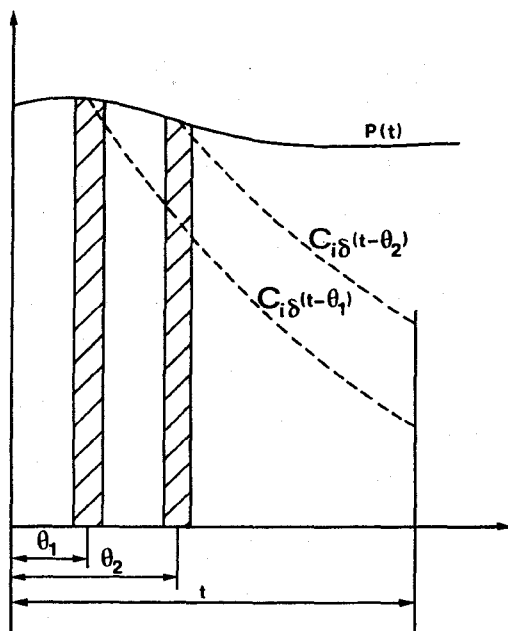
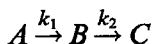


Fig. 2. The time evolution of the total concentration C_i at a given instant t (see text).

Some particular cases of interest will now be discussed.

Consecutive first-order reactions

Consider the simple consecutive mechanism



and let the initial concentrations of A , B and C be A_0 , 0 and 0, respectively. The time evolution of A , B and C in response to δ -production of each are dictated by their routes of disappearance,

$$A_\delta(t) = \exp(-k_1 t), \quad (32)$$

$$B_\delta(t) = \exp(-k_2 t), \quad (33)$$

$$C_\delta(t) = 1. \quad (34)$$

On the other hand, the production rates are

$$P_A = A_0 \delta(t), \quad (35)$$

$$P_B = k_1 A, \quad (36)$$

$$P_C = k_2 B, \quad (37)$$

Now, the direct use of eq. (30) yields

$$A = P_A \otimes A_\delta(t) = A_0 \delta(t) \otimes \exp(-k_1 t) = A_0 \exp(-k_1 t), \quad (38)$$

$$B = k_1 A \otimes B_\delta(t) = k_1 A_0 \exp(-k_1 t) \otimes \exp(-k_2 t), \quad (39)$$

$$C = k_2 B \otimes C_\delta(t) = k_1 k_2 A_0 \exp(-k_1 t) \otimes \exp(-k_2 t) \otimes 1. \quad (40)$$

From the definition of convolution and by performing the convolution integrals, one obtains with $\Delta k = k_2 - k_1$

$$\exp(-k_1 t) \otimes \exp(-k_2 t) = \frac{\{\exp(-k_1 t) - \exp(-k_2 t)\}}{\Delta k} \quad (41)$$

and, by making $k_1 = 0$ and knowing that convolution obeys the commutativity property,

$$\exp(-k_2 t) \otimes 1 = \frac{1 - \exp(-k_2 t)}{k_2}, \quad (42)$$

so that

$$\exp(-k_1 t) \otimes \exp(-k_2 t) \otimes 1 = \frac{1}{k_2} \{\exp(-k_1 t) \otimes 1 - \exp(-k_1 t) \otimes \exp(-k_2 t)\}, \quad (43)$$

hence

$$A = A_0 \exp(-k_1 t), \quad (44)$$

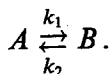
$$B = \frac{A_0 k_1 \{\exp(-k_1 t) - \exp(-k_2 t)\}}{\Delta k}, \quad (45)$$

$$C = A_0 \left\{ 1 - \exp(-k_1 t) - \frac{k_1 [\exp(-k_1 t) - \exp(-k_2 t)]}{\Delta k} \right\}. \quad (46)$$

Note that for non-zero initial concentrations of B and C the treatment is identical, but the respective production rates are added with a term similar to eq. (35), e.g. for non-zero B one has $P_B = B_0 \delta(t) + k_1 A$. Eqs. (44)–(46) are well known but were obtained here without solving any differential equations.

Reversible first-order reactions

Consider now the scheme



The δ -production responses are, as before,

$$A_\delta(t) = \exp(-k_1 t), \quad (47)$$

$$B_\delta(t) = \exp(-k_2 t), \quad (48)$$

and the production rates are

$$P_A = A_0 \delta(t) + k_2 B, \quad (49)$$

$$P_B = B_0 \delta(t) + k_1 A. \quad (50)$$

Combining eqs. (47)–(50) one obtains

$$A = A_0 \exp(-k_1 t) + k_2 B \otimes \exp(-k_1 t), \quad (51)$$

$$B = B_0 \exp(-k_2 t) + k_1 A \otimes \exp(-k_2 t). \quad (52)$$

The time evolutions of A and B are not independent, as eqs. (51) and (52) are coupled. Their separation is easily done by the use of Laplace transforms. Knowing that the Laplace transform of the convolution product $f \otimes g$ is the product of individual Laplace transforms, i.e., $\overline{f \otimes g} = \bar{f} \bar{g}$, that the Laplace transform is a linear operator and that the transform of $a \exp(-bt)$ is $a/(s+b)$, one gets

$$\bar{A} = \frac{A_0}{s+k_1} + \frac{k_2}{s+k_1} \bar{B}, \quad (53)$$

$$\bar{B} = \frac{B_0}{s+k_2} + \frac{k_1}{s+k_2} \bar{A}. \quad (54)$$

This algebraic system is solved to yield with $k = k_1 + k_2$

$$\bar{A} = \frac{A_0}{k} \left(\frac{k_2}{s} + \frac{k_1}{s+k} \right) + B_0 \frac{k_2}{k} \left(\frac{1}{s} - \frac{1}{s+k} \right), \quad (55)$$

$$\bar{B} = \frac{B_0}{k} \left(\frac{k_1}{s} + \frac{k_2}{s+k} \right) + A_0 \frac{k_1}{k} \left(\frac{1}{s} - \frac{1}{s+k} \right). \quad (56)$$

After Laplace inversion, one finally obtains

$$A = \frac{A_0}{k} [k_2 + k_1 \exp(-kt)] + B_0 \frac{k_2}{k} [1 - \exp(-kt)], \quad (57)$$

$$B = \frac{B_0}{k} [k_1 + k_2 \exp(-kt)] + A_0 \frac{k_1}{k} [1 - \exp(-kt)]. \quad (58)$$

Again, eqs. (57) and (58), already obtained with the matrix eigenvalue method [10], are well known but were obtained without solving differential equations.

Kinetics in open systems

The previous reasoning applies equally well to open systems. In fact, input flow of reactants from the outside is incorporated in the production terms whereas output flow of both reactants and products affects only the δ -responses. Consider a constant volume ideal continuous flow stirred tank reactor (CSTR) where reaction



occurs, no A being initially present in the reactor. A flow of A solution, with concentration A_0 , enters the reactor (which has a constant volume V) at a constant volume rate Φ . The output flow has also the same volume rate, Φ . Then,

$$A_\delta(t) = \exp\{-(k + \Phi/V)t\}. \quad (59)$$

Also, assuming instantaneous mixing,

$$P_A = A_0\Phi/V, \quad (60)$$

and for product B

$$B_\delta(t) = \exp(-\Phi t/V), \quad (61)$$

$$P_B = kA, \quad (62)$$

hence,

$$A = A_0 \frac{\Phi}{V} \otimes \exp\left\{-\left(k + \frac{\Phi}{V}\right)t\right\}, \quad (63)$$

$$B = kA \otimes \exp\left(-\frac{\Phi}{V}t\right) = kA_0 \frac{\Phi}{V} \otimes \exp\left\{-\left(k + \frac{\Phi}{V}\right)t\right\} \otimes \exp\left(-\frac{\Phi}{V}t\right) \quad (64)$$

or, finally,

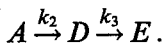
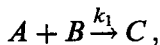
$$A = \frac{A_0}{\frac{V}{\Phi}k + 1} \left[1 - \exp\left\{-\left(k + \frac{\Phi}{V}\right)t\right\}\right], \quad (65)$$

$$B = \frac{kA_0}{\frac{V}{\Phi}k + 1} \left[\frac{V}{\Phi} \left(1 - \exp\left\{-\frac{\Phi}{V}t\right\}\right) - \frac{1}{k} \left(\exp\left(-\frac{\Phi}{V}t\right) - \exp\left\{-\left(k + \frac{\Phi}{V}\right)t\right\}\right) \right]. \quad (66)$$

Note that non-zero steady-state concentrations of A and B are attained for long times, as expected. The time evolution of A and B in an open system of the type $A + C \rightarrow B$, with reactant $C = C_0 = \text{const.}$ being absent from input flow, is described by eqs. (65) and (66) but with the inclusion of a term C_0 that multiplies with k .

Mechanisms with bimolecular elementary steps

Complex kinetic schemes frequently contain bimolecular steps. If these cannot be assumed to be of first order, the present approach is not applicable to the species that decay by those steps. Even then, the convolution approach may be of some interest. Consider for instance the scheme, whose solutions are already complex [5],



Species A and B cannot in general be handled by the present approach, as they participate in a bimolecular step. But species C , D and E can still be related with A and B by this approach. From the above enunciated rules, one can write directly the following integral relations between concentrations:

$$C = (k_1 AB) \otimes 1, \quad (67)$$

$$D = (k_2 A) \otimes \exp(-k_3 t), \quad (68)$$

$$E = (k_3 D) \otimes 1 = k_2 k_3 A \otimes \exp(-k_3 t) \otimes 1. \quad (69)$$

Integral relations of this type may be of importance for the experimental determination of rate constants. For example, if the time evolutions are known from experiment, the rate coefficients can be written as

$$k_1 = \frac{C}{(AB) \otimes 1} = \frac{C(t)}{\int_0^t A(u)B(u)du}, \quad (70)$$

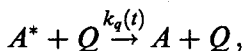
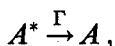
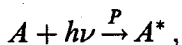
$$k_3 = \frac{E(t)}{D \otimes 1} = \frac{E(t)}{\int_0^t D(u)du}, \quad (71)$$

$$k_2 = \frac{D(t)}{A \otimes \exp(-k_3 t)} = \frac{D(t)}{A \otimes \exp[-E(t)t / \int_0^t D(u)du]}. \quad (72)$$

As far as the authors are aware, this method has never been used for the calculation of rate constants.

Fluorescence quenching

Consider the following scheme for fluorescence quenching in solution:



where the molecule A after being electronically excited by photon absorption with a production rate P (related to the incident photon intensity) decays with intrinsic lifetime $\tau = 1/\Gamma$ owing to the unimolecular radiative and nonradiative processes and also by a bimolecular quenching process with rate coefficient $k_q(t)$. The quencher concentration is usually much larger than that of excited molecules A^* but if the quenching process is diffusion controlled, the rate coefficient is time dependent and to a good approximation given by the Smoluchowski equation [16]

$$k_{q\delta}(t) = 4\pi DN_A R_e \left[1 + \frac{R_e}{\sqrt{\pi Dt}} \right] = a + \frac{b}{\sqrt{t}}, \quad (73)$$

where D is the sum of the diffusion coefficients of A^* and Q , N_A is the Avogadro's number and R_e the encounter radius ($R_e = r_{A^*} + r_Q$), the quenching reaction being supposed to occur instantaneously. This time-dependence at early times results from the reaction of pairs of molecules (A^* , Q) that are in close proximity and react very fast. After time $t > R_e^2/\pi D$, a stationary distribution of quenchers around the excited molecules has built up owing to molecular diffusion, and the quenching rate coefficient attains a stationary value given by

$$k_{q\delta}(\infty) = 4\pi DN_A R_e. \quad (74)$$

The time evolution of A^* , after δ -production, is (see eq. (29))

$$A^*_\delta = \exp(-\Gamma t) \exp\left(-\int_0^t k_{q\delta}(u) du\right) \quad (75)$$

and for a general production rate $P(t)$

$$A^* = P \otimes A^*_\delta = \int_0^t P(t-\theta) \exp\{-(\Gamma\theta + aQ\theta + 2bQ\theta^{1/2})\} d\theta. \quad (76)$$

A photostationary concentration of A^* , A^*_{ss} is expected for long times when the production rate is constant. This stationary concentration is given in the limit $t \rightarrow \infty$ for a constant production term, P_0 ,

$$A_{ss}^* = \lim_{t \rightarrow \infty} A^*(t) = \frac{P_0 \tau (1 - \sqrt{\pi} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda))}{1 + a \tau Q} \quad (77)$$

with

$$\lambda = \frac{a \tau Q R_e}{\sqrt{\pi(1 + a \tau Q) \tau D}} \quad (78)$$

and $\operatorname{erfc}(x)$ is the complementary error function

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-z^2) dz, \quad (79)$$

a photostationary rate constant $k_{q,ss}$ can be defined by

$$k_{q,ss} = \frac{1}{Q} \left(\frac{P_0}{A_{ss}^*} - \Gamma \right) = \left(a + \frac{\sqrt{\pi} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)}{Q \tau} \right) / \left(1 - \sqrt{\pi} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda) \right). \quad (80)$$

This being different from the long time limit of the time dependent quenching rate coefficient $k_q(t)$, eq. (74). Indeed, for a general time dependent rate constant $k(t)$, it can be shown [17, 18], that the correct time dependent rate coefficient is given by

$$k(t) = \frac{P \otimes (k_\delta A_\delta)}{P \otimes A_\delta}, \quad (81)$$

where $k_\delta(t)$ is the rate constant for delta production and $A_\delta(t)$ the respective time evolution of A (see eqs. (29) and (75)). From this equation, the steady-state rate coefficient is obtained as

$$k_{ss} = \frac{\int_0^\infty k_\delta(t) A_\delta(t) dt}{\int_0^\infty A_\delta(t) dt}. \quad (82)$$

This is an alternative way for the calculation of eq. (80).

4. Conclusion

The aim of the present work was to show the interest and range of applicability of the matrix and convolution approaches. These two methods find several applications in chemical kinetics of complex systems and in photochemical kinetics. The mechanical method to construct the rate matrices of any order and complexity reduces the task of writing the rate equations, a very tedious and error prone procedure (for systems with more than 3 reactions), to the level of a recipe. Furthermore, the matrix approach allows a general view of the integration of rate equations and introduces, for some 1st order \mathbf{K} matrices, the possibility to use the eigenvalue method for the solution of the kinetic equation with a formalism that is very similar

to the one used in quantum chemistry. On the other hand, the convolution approach allows the writing of the mole balance equations directly in the integrated form, whenever the decay of a species is effectively of first order. The examples here presented are simple kinetic schemes, whose results are well known. They served, however, to introduce the two approaches and to show their structure and straightforwardness.

The final system discussed with the convolution approach contained a mixture of unimolecular and bimolecular steps. In cases like this, all species disappearing through first order processes can still be handled by the convolution mechanism, and this may allow the direct estimation of rate constants or the comparison between experimental and calculated time evolutions. More complex cases, where the rate coefficients are time-dependent, including excimer formation and radiationless energy transfer can also be treated by the same formalism, non-trivial results being then obtained [13].

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