The Integration of Kinetic Rate Equations by Matrix Methods

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The evaluation of the kinetic rate constants of a given kinetic scheme is usually done by a fitting procedure of the experimental results to the integral kinetic equations. For this reason an important part of chemical kinetics courses is devoted to the integration of the rate equations. The usual presentation of this topic (1-3) consists in studying several particular cases, namely *first-order, second-order, first-order consecutive, reversible first-order*, etc. While this is quite necessary, it may leave the student with the impression that each case is somewhat unique.

The aim of this paper is to present a general approach based on a matrix formulation of the differential kinetic equations. This subject is only briefly treated in basic texts of chemical kinetics (2, 4). In the first part of the paper we present a general analytical solution for systems composed only of unimolecular steps. The method presented is exemplified in the case of two consecutive unimolecular reactions. In the second part the general case of kinetic systems composed by steps of any order is analyzed. Numerical methods are presented in terms of the same matrix formulation. Numerical calculations are performed for a real complex kinetic system and the results obtained are discussed.

The Matrix Formulation for Unimolecular Systems

It is well known that even moderately complex kinetic systems present very complicated integral solutions. In most cases closed form solutions are even impossible, and one is forced to resort to implicit equations or infinite series (3, 5), let alone numerical integration.

Unfortunately, no criterion exists that enable us to answer the question: is this reaction kinetic scheme amenable to a solution in terms of elementary functions? However there is a class of kinetic systems known to always prompt the affirmative: those solely composed by unimolecular steps (6).

Let X_i represent the concentration of species i. If there are n such species, the general set of rate equations for a unimolecular system will be

$$\frac{dX_1}{dt} = k_{11}X_1 + k_{12}X_2 + \ldots + k_{1n}X_n$$

$$\frac{dX_2}{dt} = k_{21}X_1 + k_{22}X_2 + \ldots + k_{2n}X_n$$

$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots \quad (1)$$

$$\frac{dX_n}{dt} = k_{n1}X_1 + k_{n2}X_2 + \ldots + k_{nn}X_n$$

or, in matrix form

$$\frac{d\mathbf{X}}{dt} = \mathbf{KX} \quad (2)$$

where $\mathbf{X}$ (state vector) and $\mathbf{K}$ (rate matrix) are

$$\mathbf{X} = \begin{bmatrix} X_1 \\ X_2 \\ \cdot \\ \cdot \\ \cdot \\ X_n \end{bmatrix} \quad \mathbf{K} = \begin{bmatrix} k_{11} & k_{12} & \cdot & \cdot & \cdot & k_{1n} \\ k_{21} & k_{22} & \cdot & \cdot & \cdot & k_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ k_{n1} & k_{n2} & \cdot & \cdot & \cdot & k_{nn} \end{bmatrix} \quad (3)$$

The solution of the differential eq 2 is similar to the corresponding scalar equation (7), i.e.,

$$\mathbf{X}(t) = \exp(\mathbf{K}t)\mathbf{X}(0) \quad (4)$$

where the exponential of the matrix $(\mathbf{K}t)$ is defined by the familiar expansion

$$\exp(\mathbf{K}t) = \mathbf{U} + \mathbf{K}t + (\mathbf{K}t)^2/2! + \ldots \quad (5)$$

$\mathbf{U}$ being the unit matrix of order n.

The matrix $\exp(\mathbf{K}t)$ is called the state transition matrix, and denoted by $\Phi(t)$, in a different context (7). We will conform to this usage here. In order to solve eq 2 we need to compute the state transition matrix. There are several methods to perform this: The calculation of successive powers of $\mathbf{K}$, followed by the use of eq 5, is perhaps the most straightforward. However, this is a rather cumbersome procedure. A general method, based on the Cayley–Hamilton theorem (8), allows the reduction of the infinite series (eq 5) to

$$\Phi(t) = \frac{1}{\Delta} [\Delta_0 \mathbf{U} + \Delta_1 (\mathbf{K}t)^2 + \ldots + \Delta_{n-1}(\mathbf{K}t)^{n-1}] \qquad (6)$$

where Δ is the Vandermonde determinant,

$$\Delta = \det \begin{bmatrix} 1 & \mu_1 & \mu_1^2 & \cdots & \mu_1^{n-1} \\ 1 & \mu_2 & \mu_2^2 & \cdots & \mu_2^{n-1} \\ \cdot & \cdot & \cdot & & \cdot \\ 1 & \mu_n & \mu_n^2 & \cdots & \mu_n^{n-1} \end{bmatrix} \qquad (7)$$

and Δ_i is the determinant obtained from eq 7 by substituting $\exp(\mu_1), \exp(\mu_2), \ldots \exp(\mu_n)$, for $\mu_1{}^i, \mu_2{}^i, \ldots \mu_n{}^i$. The μ_i values are related to the eigenvalues of $\mathbf{K}$ by

$$\mu_i = \lambda_i t \qquad (i = 1, 2, \ldots, n) \qquad (8)$$

with the eigenvalues obtained from the equation

$$\det(\mathbf{K} - \lambda \mathbf{U}) = 0 \qquad (9)$$

if the eigenvalues of $\mathbf{K}$ are all distinct, eq 6 can be recast in a simpler form

$$\Phi(t) = \mathbf{M}_1 \exp(\lambda_1 t) + \mathbf{M}_2 \exp(\lambda_2 t) + \ldots + \mathbf{M}_n \exp(\lambda_n t) \qquad (10)$$

where the $\mathbf{M}_i$ are matrices related to $\mathbf{K}$ and its eigenvalues by

$$M_i = \prod_{\substack{j=1 \\ j \neq i}}^{n} \frac{\mathbf{K} - \lambda_j \mathbf{U}}{\lambda_i - \lambda_j} \qquad (i = 1, 2, \ldots, n) \qquad (11)$$

substitution of eq 10 in eq 4 yields

$$\mathbf{X}(t) = \mathbf{C}_1 \exp(\lambda_1 t) + \mathbf{C}_2 \exp(\lambda_2 t) + \ldots + \mathbf{C}_n \exp(\lambda_n t) \qquad (12)$$

where the $\mathbf{C}_i$ are column vectors

$$\mathbf{C}_i = \mathbf{M}_i \mathbf{X}(0) \qquad (i = 1, 2, \ldots, n) \qquad (13)$$

Computation of the eigenvalues of the rate matrix $\mathbf{K}$, together with that of the $\mathbf{C}_i$ vectors gives the solution of eq 2 in the form of eq 12. Calculation of the $\mathbf{C}_i$ vectors by use of eqs 11 and 13 is not usually the easiest procedure. In fact, substitution of eq 12 in both sides of eq 2 gives

$$\mathbf{K}\,\mathbf{C}_i = \lambda_i\,\mathbf{C}_i \qquad (i = 1, 2, \ldots, n) \qquad (14)$$

which shows that these vectors are eigenvectors of the rate matrix. Therefore, they may be directly obtained as eigenvectors of $\mathbf{K}$ and are completely defined, apart from a multiplicative constant (if $\mathbf{C}_i$ verifies eq 14, then $\alpha \mathbf{C}_i$ also verifies it, α being a scalar constant). In this way, eq 12 can be rewritten as

$$\mathbf{X}(t) = \alpha_1 \mathbf{C}_1^0 \exp(\lambda_1 t) + \alpha_2 \mathbf{C}_2^0 \exp(\lambda_2 t) + \ldots + \alpha_n \mathbf{C}_n^0 \exp(\lambda_n t) \qquad (15)$$

where the $\mathbf{C}_i{}^0$ are arbitrarily chosen eigenvectors of $\mathbf{K}$ (asso-

ciated with λ_i) and α_i unknown scalar constants. These are determined by the initial conditions,

$$\mathbf{X}(0) = \alpha_1 \mathbf{C}_1^0 + \alpha_2 \mathbf{C}_2^0 + \ldots + \alpha_n \mathbf{C}_n^0 \qquad (16)$$

which is a system of n equations in n unknowns. This system can be written in a matrix form,

$$\mathbf{C}_0 \alpha = \mathbf{X}_0 \qquad (17)$$

where $\mathbf{C}_0$ is the modal matrix, whose columns are the eigenvectors $\mathbf{C}_i{}^0$, and α is the vector of the scalar coefficients.

$$\mathbf{C}_0 = \begin{bmatrix} C_{11}^0 & C_{21}^0 & \cdots & C_{n1}^0 \\ C_{12}^0 & C_{22}^0 & \cdots & C_{n2}^0 \\ \cdot & \cdot & & \cdot \\ C_{1n}^0 & C_{2n}^0 & \cdots & C_{nn}^0 \end{bmatrix} \qquad \alpha = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \cdot \\ \alpha_n \end{bmatrix} \qquad (18)$$

hence
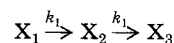
$$\alpha = \mathbf{C}_0^{-1} \mathbf{X}(0) \qquad (19)$$

Therefore the solution of eq 2 (eq 15) is obtained in the following three steps:

(i) Compute the eigenvalues of $\mathbf{K}$ (eq 9)
(ii) Compute a set of eigenvectors of $\mathbf{K}$ (eq 14)
(iii) Compute the scalar coefficients (eq 19)

A Simple Example

Let us consider the following example of a consecutive reaction with two unimolecular steps

$$X_1 \xrightarrow{k_1} X_2 \xrightarrow{k_1} X_3$$

the system of rate equations is

$$\frac{d}{dt}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \qquad (20)$$

and therefore

$$\mathbf{K} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} \qquad (21)$$

the eigenvalues of $\mathbf{K}$ are easily found to be $\lambda_1 = -k_1$, $\lambda_2 = -k_2$ and $\lambda_3 = 0$, and a set of particular eigenvectors to be

$$\mathbf{C}_1^0 = \begin{bmatrix} k_2 - k_1 \\ k_1 \\ -k_2 \end{bmatrix} \qquad \mathbf{C}_2^0 = \begin{bmatrix} 0 \\ 1 \\ -1 \end{bmatrix} \qquad \mathbf{C}_3^0 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \qquad (22)$$

hence

$$\alpha = \begin{bmatrix} \dfrac{X_1(0)}{k_2 - k_1} \\ X_2(0) - \dfrac{k_1}{k_2 - k_1} X_1(0) \\ X_1(0) + X_2(0) + X_3(0) \end{bmatrix} \qquad (23)$$

and by use of eq 15, the solution is

$$\mathbf{X}(t) = \begin{bmatrix} X_1(0) \exp(-k_1 t) \\ \dfrac{k_1 X_1(0)}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)) + X_2(0) \exp(-k_2 t) \\ \left(1 + \dfrac{1}{k_2 - k_1}(k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t))\right) X_1(0) + (1 - \exp(-k_2 t)) X_2(0) + X_3(0) \end{bmatrix} \qquad (24)$$

The Case of Degenerate Eigenvalues

If there are degenerate eigenvalues, eq 12 is no longer applicable. From eq 6 it may be shown that if λ_i is n times degenerate, there will be terms in $\exp(\lambda_i t)$, $t\exp(\lambda_i t)$, ..., $t^{n-1} \exp(\lambda_i t)$. For instance, if one of the eigenvalues, λ_1 say, is double degenerate, eq 12 is replaced by

$$\mathbf{X}(t) = (\mathbf{C}_1' + \mathbf{C}_1 t) \exp(\lambda_1 t) + \mathbf{C}_2 \exp(\lambda_2 t) + \ldots + \mathbf{C}_{n-1} \exp(\lambda_{n-1} t) \qquad (25)$$

where the $\mathbf{C}_i$ are eigenvectors and $\mathbf{C}_1'$ verifies

$$\lambda_1 \mathbf{C}_1' + \mathbf{C}_1 = \mathbf{K}\,\mathbf{C}_1' \qquad (26)$$

as can be obtained by substituting eq 25 on both sides of eq 2. In the above example, this case arrives if $k_1 = k_2 = k$. One then obtains, either by use of eq 6 or by use of eq 25

$$\mathbf{X}(t) = \begin{bmatrix} X_1(0)\,\exp(-kt) \\ (kX_1(0)t + X_2(0))\,\exp(-kt) \\ X_1(0) + X_2(0) + X_3(0) - (kX_1(0)t + X_1(0) + X_2(0))\,\exp(-kt) \end{bmatrix} \qquad (27)$$

As stated before, if the kinetic system is composed solely of unimolecular steps, an analytical solution always exists. In practice the solution cannot be obtained in many cases due to the impossibility of extracting the roots of the characteristic polynomial of $\mathbf{K}$, i.e., of obtaining its eigenvalues.

Some interesting applications where the explicit solutions are obtainable, are given by Carpenter (9).
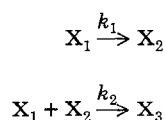
The formalism presented here is quite general and can be found in different subjects like relaxation kinetics (10) and radiationless energy transfer between identical molecules (11).

Systems of Any Order

In the most general case (elementary steps of any order) the rate equations may be written

$$\frac{dX_1}{dt} = k_{11}(t)X_1 + k_{12}(t)X_2 + \ldots + k_{1n}(t)X_n$$

$$\frac{dX_2}{dt} = k_{21}(t)X_1 + k_{22}(t)X_2 + \ldots + k_{2n}(t)X_n$$

$$\cdots \cdots \cdots \cdots \cdots \cdots \qquad (28)$$

$$\frac{dX_n}{dt} = k_{n1}(t)X_1 + k_{n2}(t)X_2 + \ldots + k_{nn}(t)X_n$$

where the pseudoconstants $k_{ij}(t)$ contain the concentration of species other than j. For example, the system

$$X_1 \xrightarrow{k_1} X_2$$

$$X_1 + X_2 \xrightarrow{k_2} X_3$$

gives

$$\frac{d}{dt}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} = \begin{bmatrix} -k_1 & -k_2 X_1 & 0 \\ k_1 & -k_2 X_1 & 0 \\ 0 & k_2 X_1 & 0 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \qquad (29)$$

or

$$\frac{d}{dt}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} = \begin{bmatrix} -(k_1 + k_2 X_2) & 0 & 0 \\ k_1 - k_2 X_2 & 0 & 0 \\ k_2 X_2 & 0 & 0 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \qquad (30)$$

The rate matrix is then, in general not unique (an infinite number of matrices can be written for the above example), and is a function of time

$$\frac{d\mathbf{X}}{dt} = \mathbf{K}(t)\mathbf{X} \qquad (31)$$

Since the dependence of $\mathbf{K}$ on time is implicit (via concentrations) exact integration of eq 31 is generally impossible. Solutions for a large number of cases are nevertheless known and can be found in refs 1–6. For complex systems approximations are often invoked (namely the steady-state and preequilibrium approximations), in order to simplify the mathematics (12–18). However, the general applicability of such approximations was questioned by several authors (15–18). When a solution valid for all times and species involved is desired, other methods, namely numerical integration, should be applied. The simplest numerical procedure is to approximate $d\mathbf{X}/dt$ by $\Delta\mathbf{X}/\Delta t$ (Euler's method).

$$\frac{\Delta\mathbf{X}}{\Delta t} = \frac{\mathbf{X}(t + \Delta t) - \mathbf{X}(t)}{\Delta t} = \mathbf{K}(t)\mathbf{X}(t) \qquad (32)$$

hence[1],

$$\mathbf{X}(t + \Delta t) = [\mathbf{U} + \mathbf{K}(t)\Delta t]\mathbf{X}(t) \qquad (33)$$

Repeated application of eq 33 (with constant or variable time increment Δt), assuming $\mathbf{X}(0)$ known, allows the calculation of the concentration of all species at any instant. This method has a local error of the order $(\Delta t)^2$, owing to the truncation of the Taylor series expansion, that restricts its accuracy. The global error (due to the accumulated errors in each integration step) is difficult to estimate. Obviously it depends on how $\mathbf{X}(t)$ behaves and how close the approximations are in different steps. Oscillations in $\mathbf{X}(t)$ can make the errors cancel each other; conversely instability in the integration method can lead to large global errors even with a very small local error. Instability is a very important problem in chemical kinetics (*stiff* systems), whenever the rates differ by orders of magnitude and the variation in time of the concentration of some species is very small (20, 21). A detailed analysis of the problem is out of the scope of this paper. Sophisticated numerical methods and the corresponding software packages are accessible (22–24).

Besides Euler's method, other simple methods of integration are known, and we refer here to the Runge–Kutta method (25) where a better accuracy can be obtained using a larger integration step, reducing in this way the computation time. In this method the step is subdivided and $\mathbf{K}(t)$ is computed at selected points in each subinterval. An approximate formula is used to calculate $\mathbf{X}(t)$ for each step. Different orders for this method are known depending on the number of subdivisions used. For a differential equation of the form

$$\frac{dy}{dx} = f(x, y) \qquad (34)$$

the Runge–Kutta method of fourth order gives,

$$y(x + \Delta x) = y(x) + \Delta x/6(k_1 + 2k_2 + 2k_3 + k_4) \qquad (35)$$

with

$$k_1 = f(x, y)$$

$$k_2 = f(x + \Delta x/2, y + k_1/2) \qquad (36)$$

$$k_3 = f(x + \Delta x/2, y + k_2/2)$$

$$k_4 = f(x + \Delta x, y + k_3)$$

the method can be extended in order to solve matrix eq 31, giving, in a compact form,

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[1] Formosinho et al. (*19*) using "Markov chains" arrive in a more complicated way at a similar result. Their method is therefore purely deterministic.

$$\mathbf{X}(t + \Delta t) = \mathbf{D}(t)\mathbf{X}(t) \tag{37}$$

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

$$\mathbf{D}(t) = \mathbf{U} + \Delta t/6[\mathbf{K}(t) + 2\mathbf{K}_1(t)\mathbf{A}(t) + 2\mathbf{K}_2(t)\mathbf{B}(t) + \mathbf{K}_3(t)\mathbf{C}(t)] \tag{38}$$

with

$$\mathbf{A}(t) = \mathbf{U} + \mathbf{K}(t)\Delta t/2$$

$$\mathbf{B}(t) = \mathbf{U} + \mathbf{K}_1(t)\mathbf{A}(t)\Delta t/2 \tag{39}$$

$$\mathbf{C}(t) = \mathbf{U} + \mathbf{K}_2(t)\mathbf{B}(t)\Delta t$$

and $\mathbf{K}_i$ are the matrices $\mathbf{K}$ evaluated in different points of the interval, namely

$$\mathbf{K}_1(t) = \mathbf{K}(\mathbf{A}(t)\mathbf{X}(t))$$

$$\mathbf{K}_2(t) = \mathbf{K}(\mathbf{B}(t)\mathbf{X}(t)) \tag{40}$$

$$\mathbf{K}_3(t) = \mathbf{K}(\mathbf{C}(t)\mathbf{X}(t))$$
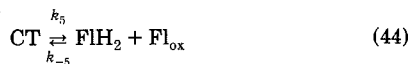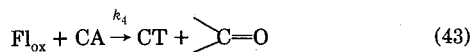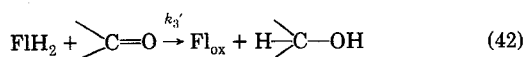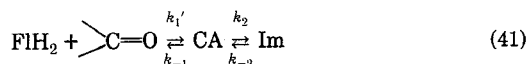
$$\mathbf{X} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix} \quad \mathbf{K} = \begin{bmatrix} -(k_1 + k_3) & k_{-1} & 0 & -k_5X_4 & \mathbf{k}_5 \\ k_1 & -(k_{-1} + k_2) & k_{-2} & -k_4X_2 & 0 \\ 0 & k_2 & -k_{-2} & 0 & 0 \\ k_3 & -k_4X_4 & 0 & -k_{-5}X_1 & \mathbf{k}_5 \\ 0 & k_4X_4 & 0 & k_{-5}X_1 & -\mathbf{k}_5 \end{bmatrix} \tag{46}$$

The matrix $\mathbf{D}(t)$ can be evaluated using eqs 39 and 40, knowing the matrix $\mathbf{K}(t)$ and the interval Δt. Once known $\mathbf{D}(t)$ for a given instant the value of $\mathbf{X}$ for the next instant ($t + \Delta t$) is straightforwardly calculated using eq 37. In this way successive applications of eq 37 allow the calculation of the time dependence of the concentration of all species.

The local error in this integration procedure is of the order $(\Delta t)^5$. When compared with Euler's method a better accuracy is in general obtained. However, this method may not be suitable for stiff systems (25) because of the prohibitively large number of steps required to maintain stability. The numerical formalisms presented are, in their matrix form, quite appropriate for computational purposes, owing to their generality and compactness[2].

Application to a Real System

We will consider here the work of Williams and Bruice (26) on the reduction of carbonyl compounds like pyruvamide by 1,5-dihydroflavines. A simplified mechanism for these reactions, is

$$FlH_2 + \overset{k_1'}{\underset{k_{-1}}{\rightleftarrows}} C{=}O \overset{k_2}{\underset{k_{-2}}{\rightleftarrows}} CA \rightleftarrows Im \tag{41}$$

$$FlH_2 + \overset{k_3'}{\longrightarrow} C{=}O \rightarrow Fl_{ox} + H{-}C{-}OH \tag{42}$$

$$Fl_{ox} + CA \overset{k_4}{\longrightarrow} CT + C{=}O \tag{43}$$

$$CT \overset{k_5}{\underset{k_{-5}}{\rightleftarrows}} FlH_2 + Fl_{ox} \tag{44}$$

The reduced flavin (FlH_2) reacts with the pyruvic substrate ($C{=}O$) to form a carbinolamide (CA) that can dehydrate to an imine (Im) in a reversible step or return to the initial reactants. The flavin can also be oxidized to Fl_{ox} by the carbonyl compound in step 3. The oxidized flavin can react with the carbinolamide to form a charge-transfer complex (CT) which dissociates to reform FlH_2 and Fl_{ox} in a reversible way. For high concentrations of the carbonyl compound the following system of differential equations can be written

$$\frac{dX_1}{dt} = -(k_1 + k_3)X_1 + k_{-1}X_2 - k_{-5}X_1X_4 + k_5X_5$$

$$\frac{dX_2}{dt} = k_1X_1 - (k_{-1} + k_2)X_2 + k_{-2}X_3 - k_4X_2X_4$$

$$\frac{dX_3}{dt} = k_2X_2 - k_{-2}X_3 \tag{45}$$

$$\frac{dX_4}{dt} = k_3X_1 - k_4X_2X_4 - k_{-5}X_1X_4 + k_5X_5$$

$$\frac{dX_5}{dt} = k_4X_2X_4 + k_{-5}X_1X_4 - k_5X_5$$

where $k_1 = k_1'$ [$>$C$=$O] and $k_3 = k_3'$ [$>$C$=$O] are pseudo-first-order rate constants and the different species are identified in the following way:

$$X_1 = FlH_2; \ X_2 = CA; \ X_3 = Im; \ X_4 = Fl_{ox}; \ X_5 = CT$$

This system of equations can be written in a matrix formulation (see eq 31) with the vectors of concentrations $\mathbf{X}$ and the rate matrix $\mathbf{K}$ given by

We perform the numerical integration with the following rate constants: $k_1 = 2.74 \times 10^{-2}$ min^{-1}, $k_{-1} = 1.51 \times 10^{-2}$ min^{-1}, $k_2 = 1.34 \times 10^{-2}$ min^{-1}, $k_{-2} = 6.31 \times 10^{-3}$ min^{-1}, $k_3 = 2.76 \times 10^{-3}$ min^{-1}, $k_4 = 2.05 \times 10^2$ M^{-1} min^{-1}, $k_5 = 1.52 \times 10^{-2}$ min^{-1}, $k_{-5} = 2.17 \times 10^2$ M^{-1} min^{-1}, and the initial concentrations [FlH_2] = 7.0×10^{-5} M and [$>$C$=$O] = 0.10 M, corresponding to case D of ref 26.

Figure 1 shows the numerical integration using Euler's method (eq 33) with an integration step of 0.5 min. The qualitative behavior of the time evolution of the concentra-
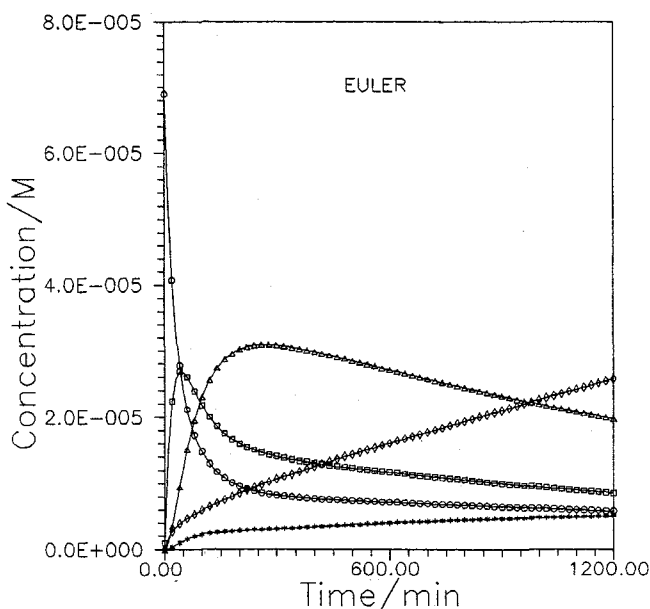
Figure 1. Concentration versus time for species of mechanism described by eqs 41–44 obtained by Euler's method with an integration step of 0.5 min and labelled at each 20 min; O, FlH$_2$; □, CA; △, Im; ◊, Fl$_{ox}$; *, CT.
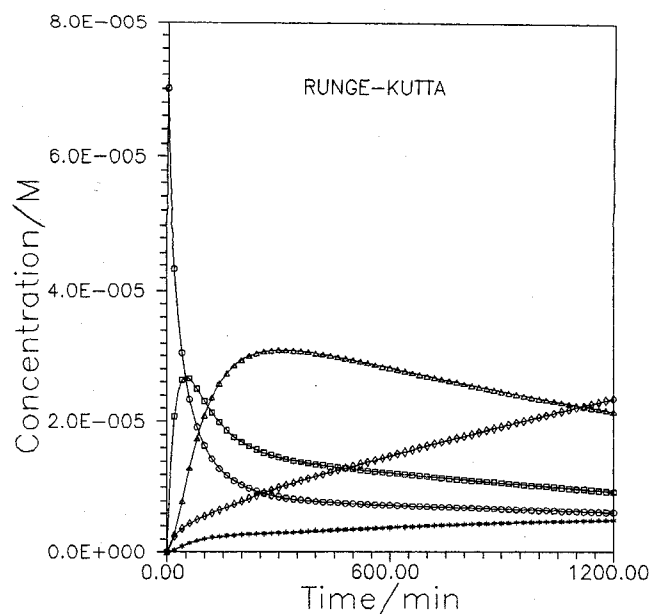
Figure 2. Concentration versus time for species of mechanism described by eqs 41–44 obtained by the fourth-order Runge–Kutta method with an integration step of 0.5 min. Curves are labelled as in Figure 1.

Figure 3. Percentage of difference between the curves of Figures 2 and 1. Symbols as in Figure 1.

tions of all species is recovered. Some difference between these results and the published profiles, obtained by analogue integration (26) can be observed. These differences remain even if a smaller step is used. In Figure 2 the profiles obtained using the fourth-order Runge–Kutta method (eq 37) with an integration step of 0.5 min are presented. The same results are obtained using a smaller step (0.2 min), which confirms that with the first integration step the method is already accurate. Figure 3 shows the plot of the percentage of difference for the time evolution of the concentration of all species as computed using Euler's and Runge–Kutta methods. A deviation is observed due mainly to the errors involved in Euler's method. The deviations are bigger at the beginning due to the large variation of the concentrations. These deviations are only slightly decreased when the integration step in the Euler's method is reduced. Comparison of the profiles obtained by the Runge–Kutta method (Fig. 2) and the ones obtained in ref 26 shows some differences especially clear for the intermediates. This probably reflects the lower precision of the analogue method (27).

Conclusions

The matrix formulation presented allows a general view of the integration of rate equations and could be included in a chemical kinetics or physical chemistry course. The required mathematical background is usually covered in undergradu-

ate algebra courses for science and engineering. This presentation can be extended to cover topics such as stiff systems integration and stability analysis.

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