

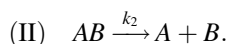
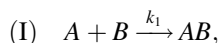
Chapter 2

Multi-Step Reactions: The Methods for Analytical Solving the Direct Problem

2.1 Developing a Mathematical Model of a Reaction

If a reaction proceeds by a large number of elementary steps and involves many different substances, developing its mathematical model “by hand” turns into a quite exhausting procedure fraught with different possible errors, especially provided complicated reaction stoichiometry. This stage can be considerably simplified by using matrix algebra suits.

Let us consider a reversible reaction consisting of two elementary steps:



A rate of each of the steps is written as

$$\vec{r} = k_1 C_A(t) C_B(t),$$

$$\bar{r} = k_2 C_{AB}(t).$$

Obviously, a reaction mathematical model is an equation system

$$\frac{dC_A(t)}{dt} = -\vec{r} + \bar{r} = -k_1 C_A(t) C_B(t) + k_2 C_{AB}(t),$$

$$\frac{dC_B(t)}{dt} = -\vec{r} + \bar{r} = -k_1 C_A(t) C_B(t) + k_2 C_{AB}(t),$$

$$\frac{dC_{AB}(t)}{dt} = \vec{r} - \bar{r} = k_1 C_A(t) C_B(t) - k_2 C_{AB}(t).$$

Let us define a *stoichiometric matrix* $\underline{\underline{\alpha}}$ for the given kinetic scheme as

$$\underline{\underline{\alpha}} = \begin{bmatrix} -1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}.$$

The number of rows in a stoichiometric matrix corresponds to the number of elementary steps and the number of columns is equal to the total number of substances taking part in a reaction. Each matrix element is a stoichiometric factor of a definite substance at a given step. At the same time, a minus sign is ascribed to stoichiometric factors of reactants and ones of products have a positive sign. If a substance is not involved in a given stage, a corresponding stoichiometric factor is equal to zero. Thus, the middle column of the stoichiometric matrix reflects participation of substance *B* in the overall process: it is consumed at the step (I) and accumulated at the step (II). Let us place expressions for the rates of each of the steps in a *rate vector* $\underline{r}$

$$\underline{r} = \begin{bmatrix} \vec{r} \\ \bar{r} \end{bmatrix} = \begin{bmatrix} k_1 C_A C_B \\ k_2 C_{AB} \end{bmatrix}.$$

Let us now find a product of the transposed matrix $\underline{\underline{\alpha}}$ and the vector $\underline{r}$

$$\underline{\underline{\alpha}}^T \cdot \underline{r} = \begin{bmatrix} -1 & 1 \\ -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} k_1 C_A(t) C_B(t) \\ k_2 C_{AB}(t) \end{bmatrix} = \begin{bmatrix} -k_1 C_A(t) C_B(t) + k_2 C_{AB}(t) \\ k_1 C_A(t) C_B(t) - k_2 C_{AB}(t) \\ k_1 C_A(t) C_B(t) - k_2 C_{AB}(t) \end{bmatrix}.$$

It is easy to see that this yields a vector formed by right parts of a differential equation system for a kinetic scheme under consideration.

Thereby, a kinetic equation for a multi-step reaction in a matrix form is written as:

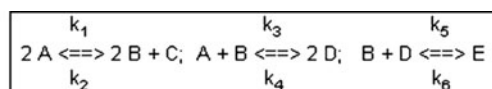
$$\frac{d}{dt} \underline{\underline{C}}(t) = \underline{\underline{\alpha}}^T \cdot \underline{r}(t). \quad (2.1)$$

Naturally, the above multiplication of a stoichiometric matrix and a rate vector can be performed by suits of mathematical packages. Figure 2.1 shows the operation sequence of such automatic developing the mathematical model of the considered reaction in the Mathcad environment.

Another way of developing a mathematical model can also be indicated. If an overall chain of conversions contains reversible steps, they can be considered as formally elementary. As a result, dimensions of a stoichiometric matrix and a rate vector can be reduced (Fig. 2.2).

So as to perform the above operations with a stoichiometric matrix and a rate vector in Maple, it is necessary to preliminarily link the library of built-in commands and functions of linear algebra `LinearAlgebra` (Fig. 2.3).

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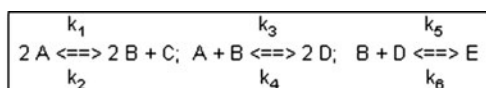
$$A := \begin{pmatrix} \text{"Steps/Reactants"} & \text{"A"} & \text{"B"} & \text{"C"} & \text{"D"} & \text{"E"} \\ \text{"."} & \text{"1"} & \text{"2"} & \text{"3"} & \text{"4"} & \text{"5"} \\ \text{"1"} & -2 & 2 & 1 & 0 & 0 \\ \text{"2"} & 2 & -2 & -1 & 0 & 0 \\ \text{"3"} & -1 & -1 & 0 & 2 & 0 \\ \text{"4"} & 1 & 1 & 0 & -2 & 0 \\ \text{"5"} & 0 & -1 & 0 & -1 & 1 \\ \text{"6"} & 0 & 1 & 0 & 1 & -1 \end{pmatrix} \quad r(k, C) := \begin{bmatrix} k_1 \cdot (C_1)^2 \\ k_2 \cdot (C_2)^2 \cdot C_3 \\ k_3 \cdot C_1 \cdot C_2 \\ k_4 \cdot (C_4)^2 \\ k_5 \cdot C_2 \cdot C_4 \\ k_6 \cdot C_5 \end{bmatrix}$$

 $\alpha := \text{submatrix}(A, 3, \text{rows}(A), 2, \text{cols}(A))$

$$\text{RHS}(k, C) := \alpha^T \cdot r(k, C) \rightarrow \begin{bmatrix} -2 \cdot k_1 \cdot (C_1)^2 + 2 \cdot k_2 \cdot (C_2)^2 \cdot C_3 - k_3 \cdot C_1 \cdot C_2 + k_4 \cdot (C_4)^2 \\ 2 \cdot k_1 \cdot (C_1)^2 - 2 \cdot k_2 \cdot (C_2)^2 \cdot C_3 - k_3 \cdot C_1 \cdot C_2 + k_4 \cdot (C_4)^2 - k_5 \cdot C_2 \cdot C_4 + k_6 \cdot C_5 \\ k_1 \cdot (C_1)^2 - k_2 \cdot (C_2)^2 \cdot C_3 \\ 2 \cdot k_3 \cdot C_1 \cdot C_2 - 2 \cdot k_4 \cdot (C_4)^2 - k_5 \cdot C_2 \cdot C_4 + k_6 \cdot C_5 \\ k_5 \cdot C_2 \cdot C_4 - k_6 \cdot C_5 \end{bmatrix}$$

Fig. 2.1 Developing the mathematical model of the reaction in Mathcad

ORIGIN := 1



$$A := \begin{pmatrix} \text{"Steps/Reactants"} & \text{"A"} & \text{"B"} & \text{"C"} & \text{"D"} & \text{"E"} \\ \text{"."} & \text{"1"} & \text{"2"} & \text{"3"} & \text{"4"} & \text{"5"} \\ \text{"1-2"} & -2 & 2 & 1 & 0 & 0 \\ \text{"3-4"} & -1 & -1 & 0 & 2 & 0 \\ \text{"5-6"} & 0 & -1 & 0 & -1 & 1 \end{pmatrix} \quad r(k, C) := \begin{bmatrix} k_1 \cdot (C_1)^2 - k_2 \cdot (C_2)^2 \cdot C_3 \\ k_3 \cdot C_1 \cdot C_2 - k_4 \cdot (C_4)^2 \\ k_5 \cdot C_2 \cdot C_4 - k_6 \cdot C_5 \end{bmatrix}$$

 $\alpha := \text{submatrix}(A, 3, \text{rows}(A), 2, \text{cols}(A))$

$$\text{RHS}(k, C) := \alpha^T \cdot r(k, C) \rightarrow \begin{bmatrix} 2 \cdot C_3 \cdot k_2 \cdot (C_2)^2 - k_3 \cdot C_1 \cdot C_2 - 2 \cdot k_1 \cdot (C_1)^2 + k_4 \cdot (C_4)^2 \\ 2 \cdot k_1 \cdot (C_1)^2 - k_3 \cdot C_1 \cdot C_2 - 2 \cdot C_3 \cdot k_2 \cdot (C_2)^2 - k_5 \cdot C_2 \cdot C_4 + k_4 \cdot (C_4)^2 + C_5 \cdot k_6 \\ (C_1)^2 \cdot k_1 - (C_2)^2 \cdot C_3 \cdot k_2 \\ C_5 \cdot k_6 - C_2 \cdot k_5 \cdot C_4 - 2 \cdot k_4 \cdot (C_4)^2 + 2 \cdot C_1 \cdot C_2 \cdot k_3 \\ C_2 \cdot C_4 \cdot k_5 - C_5 \cdot k_6 \end{bmatrix}$$

Fig. 2.2 Using the reduced stoichiometric matrix

```

[> restart;
[> with(LinearAlgebra):
[> alpha:=Matrix([[-2,2,1,0,0],[2,-2,-1,0,0],[-1,-1,0,2,0],
[> 0],[1,1,0,-2,0],[0,-1,0,-1,1],[0,1,0,1,-1]]):
[> r:=Vector([k[1]*C[1]^2,k[2]*C[2]^2*C[3],k[3]*C[1]*C[2],
[> k[4]*C[4]^2,k[5]*C[2]*C[4],k[5]*C[5]]):
[> Rhside:=Transpose(alpha).r:
[> alpha,r;

```

$$\begin{bmatrix} -2 & 2 & 1 & 0 & 0 \\ 2 & -2 & -1 & 0 & 0 \\ -1 & -1 & 0 & 2 & 0 \\ 1 & 1 & 0 & -2 & 0 \\ 0 & -1 & 0 & -1 & 1 \\ 0 & 1 & 0 & 1 & -1 \end{bmatrix}, \begin{bmatrix} k_1 C_1^2 \\ k_2 C_2^2 C_3 \\ k_3 C_1 C_2 \\ k_4 C_4^2 \\ k_5 C_2 C_4 \\ k_5 C_5 \end{bmatrix}$$

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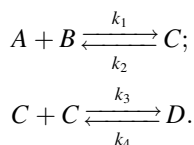
[> Rhside;

```

$$\begin{bmatrix} -2k_1 C_1^2 + 2k_2 C_2^2 C_3 - k_3 C_1 C_2 + k_4 C_4^2 \\ 2k_1 C_1^2 - 2k_2 C_2^2 C_3 - k_3 C_1 C_2 + k_4 C_4^2 - k_5 C_2 C_4 + k_5 C_5 \\ k_1 C_1^2 - k_2 C_2^2 C_3 \\ 2k_3 C_1 C_2 - 2k_4 C_4^2 - k_5 C_2 C_4 + k_5 C_5 \\ k_5 C_2 C_4 - k_5 C_5 \end{bmatrix}$$

Fig. 2.3 Developing the mathematical model using the Maple suits

The most significant stoichiometric matrix tool, which plays an important role in solving kinetic problems, is its *rank*. As it is known, a matrix rank defines the number of its linearly independent rows or columns. Using of the notion of a matrix rank allows to reduce the number of differential equations in a reaction mathematical model and, thereby, to make solving the direct and inverse kinetic problems easier. For example, let us consider a reaction scheme:



Let us develop a mathematical model for this reaction in the form of right parts of the overall differential equation system:

$$\begin{pmatrix} -1 & 1 & 1 & 0 \\ 1 & 1 & -1 & 0 \\ 0 & 0 & -2 & 1 \\ 0 & 0 & 2 & -1 \end{pmatrix}^T \cdot \begin{pmatrix} k_1 C_A C_B \\ k_2 C_C \\ k_3 C_C^2 \\ k_4 C_D \end{pmatrix} = \begin{pmatrix} -k_1 C_A C_B + k_2 C_C \\ -k_1 C_A C_B + k_2 C_C \\ -k_1 C_A C_B - k_2 C_C - 2k_3 C_C^2 + 2k_4 C_D \\ k_3 C_C^2 - k_4 C_D \end{pmatrix}.$$

If to calculate the stoichiometric matrix rank (calculation of a rank in Mathcad and Maple is implemented by means of the `rank` function), it will appear that it is equal to two. This means that it is possible to leave only two differential equations without prejudice to kinetic description of the mathematical model. Let us leave the equations describing a concentration change of substances C and D :

$$\begin{cases} dC_C/dt = -k_1 C_A C_B - k_2 C_C - 2k_3 C_C^2 + 2k_4 C_D \\ dC_D/dt = k_3 C_C^2 - k_4 C_D \end{cases}.$$

However, as we can see, the current concentrations of reactants A and B appear in one of the equations entering the obtained system. It is necessary to express them in terms of the current concentration of reactants C and D , otherwise it will be impossible to solve the equation. Such replacement can be performed using main balance relationships for complex reactions. Since we consider the process which occurs in a closed system, according to the mass conservation law we can write

$$\sum_i m_{i0} = \sum_i m_i$$

where m_{i0} and m_i are initial and current masses of the i th component, respectively. In turn, under isochoric conditions these masses are connected with initial and current concentrations C_{i0} and C_i by

$$m_{i0} = C_{i0} M_i; \quad m_i = C_i M_i,$$

where M_i is a molar mass of the i th substance taking part in a reaction. Then an equation of system material balance can be written in a matrix form as

$$\underline{\alpha} \cdot \underline{M} = \underline{0}$$

where $\underline{M}$ is a vector of molar masses and $\underline{0}$ is a zero vector.

Figure 2.4 shows the Mathcad document intended for simplifying the calculations while developing the reduced system of the differential equations. Performing the elementary symbolic transformations of the vectors and matrices involving the enumerated balance relationships allows to write the equation system in the final form:

$$\begin{cases} dC_C/dt = -k_1 (C_{A0} - C_C - 2C_D)(C_{B0} - C_C - 2C_D) - k_2 C_C - 2k_3 C_C^2 + 2k_4 C_D \\ dC_D/dt = k_3 C_C^2 - k_4 C_D \end{cases}.$$

$$\begin{aligned}
 \alpha &:= \begin{pmatrix} -1 & -1 & 1 & 0 \\ 0 & 0 & -2 & 1 \end{pmatrix} \quad \text{FullSys}\{k_1, k_2, k_3, k_4, A, B, C, D\} := \alpha^T \cdot \begin{pmatrix} k_1 \cdot A \cdot B - k_2 \cdot C \\ k_3 \cdot C^2 - k_4 \cdot D \end{pmatrix} \\
 &\quad \boxed{\text{rank}(\alpha) = 2} \\
 \alpha \cdot \begin{pmatrix} M_A \\ M_B \\ M_C \\ M_D \end{pmatrix} &\rightarrow \begin{pmatrix} -M_A - M_B + M_C \\ -2 \cdot M_C + M_D \end{pmatrix} \quad \begin{array}{l} -M_A - M_B + M_C = 0 \text{ solve, } M_C \rightarrow M_A + M_B \\ -2 \cdot M_C + M_D = 0 \end{array} \left| \begin{array}{l} \text{substitute, } M_C = M_A + M_B \\ \text{solve, } M_D \end{array} \right. \rightarrow 2 \cdot M_A + 2 \cdot M_B \\
 \sum \begin{pmatrix} m_{A0} \\ m_{B0} \\ 0 \\ 0 \end{pmatrix} &\left| \begin{array}{l} \text{substitute, } m_{A0} = A_0 \cdot M_A \\ \text{substitute, } m_{B0} = B_0 \cdot M_B \end{array} \right. \rightarrow A_0 \cdot M_A + B_0 \cdot M_B \\
 \sum \begin{pmatrix} m_A \\ m_B \\ m_C \\ m_D \end{pmatrix} &\left| \begin{array}{l} \text{substitute, } m_A = A \cdot M_A \\ \text{substitute, } m_B = B \cdot M_B \\ \text{substitute, } m_C = C \cdot (M_A + M_B) \\ \text{substitute, } m_D = 2 \cdot D \cdot (M_A + M_B) \end{array} \right. \rightarrow (C + A + 2 \cdot D) \cdot M_A + (2 \cdot D + B + C) \cdot M_B \\
 &\quad \text{collect, } M_A, M_B \\
 \text{Given} \quad A_0 &= C + A + 2 \cdot D \quad B_0 = 2 \cdot D + B + C \quad \text{Find}(A, B) \rightarrow \begin{pmatrix} A_0 - C - 2 \cdot D \\ B_0 - 2 \cdot D - C \end{pmatrix} \\
 \text{submatrix}\{\text{FullSys}\{k_1, k_2, k_3, k_4, A, B, C, D\}, 2, 3, 0, 0\} &\rightarrow \begin{pmatrix} k_1 \cdot A \cdot B - k_2 \cdot C - 2 \cdot k_3 \cdot C^2 + 2 \cdot k_4 \cdot D \\ k_3 \cdot C^2 - k_4 \cdot D \end{pmatrix} \\
 \begin{pmatrix} k_1 \cdot A \cdot B - k_2 \cdot C - 2 \cdot k_3 \cdot C^2 + 2 \cdot k_4 \cdot D \\ k_3 \cdot C^2 - k_4 \cdot D \end{pmatrix} &\left| \begin{array}{l} \text{substitute, } A = A_0 - C - 2 \cdot D \\ \text{substitute, } B = B_0 - 2 \cdot D - C \end{array} \right. \\
 &\rightarrow \begin{bmatrix} k_1 \cdot (A_0 - C - 2 \cdot D) \cdot (B_0 - 2 \cdot D - C) - k_2 \cdot C - 2 \cdot k_3 \cdot C^2 + 2 \cdot k_4 \cdot D \\ k_3 \cdot C^2 - k_4 \cdot D \end{bmatrix}
 \end{aligned}$$

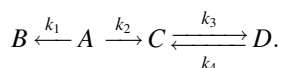
Fig. 2.4 Developing the reduced mathematical model

Thus, for multi-step reactions which involve a large number of reactants and products, corresponding mathematical models can be quite awkward. In most cases, it is not necessary to have a system of N equations for modeling N kinetic curves. Fulfillment of a condition $\text{rank}(M) < N$ means that some substances entering a general kinetic scheme can be not excluded from an initial model at all, since their kinetic curves can be calculated on the basis of information about a time-dependent concentration behaviour of other key components which have not been excluded from an overall equation system.

2.2 The Classical Matrix Method for Solving the Direct Kinetic Problem

The direct problem of chemical kinetics always has an analytical solution if a reaction mathematical model is a linear system of ordinary first-order differential equations. Sequences of elementary first-order kinetic steps, including ones complicated with reversible and competitive steps, correspond to such mathematical models. Let us mark off the *classical matrix method* from analytical methods of solving such ODE systems.

For example, suppose a kinetic scheme of a consecutive-competitive reaction with a reversible step



The mathematical model corresponding to the above scheme is

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} C_A(t) \\ C_B(t) \\ C_C(t) \\ C_D(t) \end{pmatrix} &= \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}^T \begin{pmatrix} k_1 C_A(t) \\ k_2 C_A(t) \\ k_3 C_C(t) \\ k_4 C_D(t) \end{pmatrix} \\ &= \begin{pmatrix} -(k_1 + k_2) C_A(t) \\ k_1 C_A(t) \\ k_2 C_A(t) - k_3 C_C(t) + k_4 C_D(t) \\ k_3 C_C(t) - k_4 C_D(t) \end{pmatrix}. \end{aligned}$$

Let us rewrite the vector of the right parts of the system as

$$\begin{pmatrix} -(k_1 + k_2) C_A(t) + 0 \cdot C_B(t) + 0 \cdot C_C(t) + 0 \cdot C_D(t) \\ k_1 C_A(t) + 0 \cdot C_B(t) + 0 \cdot C_C(t) + 0 \cdot C_D(t) \\ k_2 C_A(t) + 0 \cdot C_B(t) - k_3 C_C(t) + k_4 C_D(t) \\ 0 \cdot C_A(t) + 0 \cdot C_B(t) + k_3 \cdot C_C(t) - k_4 C_D(t) \end{pmatrix}.$$

Let us form a *rate constant matrix* $\underline{k}$ of the constant rates and their combinations put before the concentrations

$$\begin{pmatrix} -(k_1 + k_2) & 0 & 0 & 0 \\ k_1 & 0 & 0 & 0 \\ k_2 & 0 & -k_3 & k_4 \\ 0 & 0 & k_3 & -k_4 \end{pmatrix}.$$

It is easy to make sure that multiplication of the matrix $\underline{k}$ and the vector of current concentrations also yields the vector of the right parts of the system

$$\begin{pmatrix} -(k_1 + k_2) & 0 & 0 & 0 \\ k_1 & 0 & 0 & 0 \\ k_2 & 0 & -k_3 & k_4 \\ 0 & 0 & k_3 & -k_4 \end{pmatrix} \cdot \begin{pmatrix} C_A(t) \\ C_B(t) \\ C_C(t) \\ C_D(t) \end{pmatrix} = \begin{pmatrix} -(k_1 + k_2)C_A(t) \\ k_1C_A(t) \\ k_2C_A(t) - k_3C_C(t) + k_4C_D(t) \\ k_3C_C(t) - k_4C_D(t) \end{pmatrix}.$$

Therefore,

$$\frac{d}{dt}\underline{C}(t) = \underline{k}\underline{C}(t). \quad (2.2)$$

Equation (2.2), as (2.1), is a matrix form of a kinetic equation of a multi-step reaction. One should pay attention that a rate constant matrix always is a square matrix. A solution of (2.2) is written as

$$\underline{C}(t) = \exp(\underline{k}t)\underline{C}_0,$$

where $\underline{C}_0$ is a vector of substance initial concentrations. However, a problem of calculating a matrix $\exp(\underline{k}t)$ arises here. For the purpose of solving it, matrix algebra introduces the notions of an *eigenvalue vector* of a matrix and an *eigenvector* of a matrix. It is considered that a matrix $\underline{k}$ has an eigenvector $\underline{x}$ and a corresponding eigenvalue λ , if the condition

$$\underline{k} \cdot \underline{x}^{(i)} = \lambda_i \cdot \underline{x}^{(i)}, \quad (2.3)$$

is met. Here: λ_i is the i th element of an eigenvalues vector $\underline{\lambda}$, $\underline{x}^{(i)}$ is the i th column of a matrix of eigenvectors.

Thereby, each column of a matrix $\underline{x}$ corresponds to a quite definite eigenvalue of a matrix $\underline{k}$. Matrix algebra involves the notions of eigenvalues and eigenvectors to prove that

$$\exp(\underline{k}t) = \underline{x} \cdot \exp(\underline{\Lambda}t) \cdot \underline{x}^{-1}.$$

In the last relationship, $\underline{\Lambda}$ is a *diagonal* matrix, whose main diagonal elements are ones of an eigenvalue vector $\underline{\lambda}$. Respectively, $\exp(\underline{\Lambda}t)$ also is a diagonal matrix

$$\exp(\underline{\Lambda}t) = \begin{bmatrix} \exp(\lambda_0 t) & 0 & 0 & \dots \\ 0 & \exp(\lambda_1 t) & 0 & \dots \\ 0 & 0 & \exp(\lambda_2 t) & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix}.$$

Taking this into account, the end form of the differential equation system solution is

$$\underline{C}(t) = \underline{x} \exp(\underline{\Lambda}t) \underline{x}^{-1} \underline{C}_0.$$

Consequently, seeking analytical expressions for current concentrations of all reactants involved in a multi-step reaction is reduced to formation of matrices $\underline{x}$, $\underline{\Delta}$, and a vector of initial concentrations $\underline{C}_0$ and their multiplication in the above-stated order. Note that the multiplication order is very important since, in the general case, a product of matrices is not commutative.

Figure 2.5 demonstrates the Mathcad document designed to form all the vectors and matrices necessary for solving the direct kinetic problem. The built-in function `eigenvals` should be used to find eigenvalues of a constant rate matrix. A matrix of eigenvectors is calculated with the help of `eigenvecs`.

Matrix of rate constants

$$\begin{bmatrix} -(k_1 + k_2) & 0 & 0 & 0 \\ k_1 & 0 & 0 & 0 \\ k_2 & 0 & -k_3 & k_4 \\ 0 & 0 & k_3 & -k_4 \end{bmatrix}$$

Eigenvalue vector of matrix of rate constants

$$\text{eigenvals} \left[\begin{bmatrix} -(k_1 + k_2) & 0 & 0 & 0 \\ k_1 & 0 & 0 & 0 \\ k_2 & 0 & -k_3 & k_4 \\ 0 & 0 & k_3 & -k_4 \end{bmatrix} \right] \rightarrow \begin{bmatrix} (-k_1) - k_2 \\ 0 \\ 0 \\ (-k_3) - k_4 \end{bmatrix}$$

Diagonal matrix of elements of eigenvalue vector

$$\begin{bmatrix} \exp[(-k_1 - k_2) \cdot t] & 0 & 0 & 0 \\ 0 & \exp(0 \cdot t) & 0 & 0 \\ 0 & 0 & \exp(0 \cdot t) & 0 \\ 0 & 0 & 0 & \exp[(-k_3 - k_4) \cdot t] \end{bmatrix}$$

Eigenvector matrix

$$\text{eigenvecs} \left[\begin{bmatrix} -(k_1 + k_2) & 0 & 0 & 0 \\ k_1 & 0 & 0 & 0 \\ k_2 & 0 & -k_3 & k_4 \\ 0 & 0 & k_3 & -k_4 \end{bmatrix} \right] \rightarrow \begin{bmatrix} (k_1 + k_2) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 0 & 0 \\ (-k_1) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 0 & 1 \\ \frac{-(k_1 + k_2 - k_4)}{k_3} & -1 & \frac{1}{k_3} \cdot k_4 & 0 \\ 1 & 1 & 1 & 0 \end{bmatrix}$$

Attention! The right order of the columns

$$\begin{bmatrix} (k_1 + k_2) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 0 & 0 \\ (-k_1) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 1 & 0 \\ \frac{-(k_1 + k_2 - k_4)}{k_3} & \frac{k_4}{k_3} & 0 & -1 \\ 1 & 1 & 0 & 1 \end{bmatrix}$$

Fig. 2.5 Solving the direct kinetic problem by the matrix method: forming the necessary matrices

Note an important peculiarity of `eigenvecs`. Strictly speaking, its main destination in the Mathcad environment is symbolic but not numerical calculations. In the symbolic calculation mode, an eigenvector matrix is calculated but columns in this matrix are displayed in an arbitrary order. With each new reference to this function we get matrices with different sequence of columns in them. For this reason, it is necessary to check each time whether the i th column of an eigenvector matrix corresponds to the i th position of an eigenvalues vector. Such check should be performed by multiplication of a rate constant matrix and a chosen column of a matrix $\underline{x}$ and comparison of an obtained result with a result of multiplication of a chosen element of eigenvalue vector and the same column.

A chosen column vector of an eigenvector matrix will correspond to a chosen element of an eigenvalue vector only if equality (2.3) is fulfilled. After a performed check, a user will probably have to sort an eigenvector matrix by himself by rearranging columns in order of correspondence.

The final stage of the calculations resulting in the vector of the differential equation system solution is illustrated in Fig. 2.6.

With the help of obtained analytical expressions it is possible to draw curves for different substances provided concrete numerical values of their initial concentration as well as values of rate constants of separate steps are given.

Let us make another one remark concerning working of `eigenvecs` in Mathcad. A user can note that this function works as if in a different way in different versions of the package yielding, at first sight, different eigenvector matrices. But in reality, there is no contradiction: it is considered in linear algebra that a vector proportional to an eigenvector is also an eigenvector. This becomes obvious when carefully analyzing relationship (2.3). Eigenvector matrices obtained by means of symbolic calculations in the Mathcad 11 environment look, as a rule,

$$\begin{bmatrix} (k_1 + k_2) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 0 & 0 \\ (-k_1) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 1 & 0 \\ \frac{-(k_1 + k_2 - k_4)}{k_3} & \frac{k_4}{k_3} & 0 & -1 \\ 1 & 1 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} e^{[(-k_1) - k_2] \cdot t} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & e^{[(-k_3) - k_4] \cdot t} \end{bmatrix} \cdot \begin{bmatrix} (k_1 + k_2) \cdot \frac{k_1 + k_2 - k_3 - k_4}{k_3 \cdot k_2} & 0 & 0 & 0 \\ k_1 \cdot \frac{(-k_1) - k_2 + k_3 + k_4}{k_3 \cdot k_2} & 0 & 1 & 0 \\ \frac{-(k_1 + k_2 - k_4)}{k_3} & \frac{k_4}{k_3} & 0 & -1 \\ 1 & 1 & 0 & 1 \end{bmatrix}^{-1} \cdot \begin{pmatrix} C_{A0} \\ 0 \\ 0 \\ 0 \end{pmatrix} \rightarrow \\
 \rightarrow \begin{bmatrix} e^{[(-k_1) - k_2] \cdot t} \cdot C_{A0} \\ \left[(-k_1) \cdot \frac{e^{[(-k_1) - k_2] \cdot t}}{k_1 + k_2} + \frac{k_1}{k_1 + k_2} \right] \cdot C_{A0} \\ \left[[(-k_1) - k_2 + k_4] \cdot \frac{e^{[(-k_1) - k_2] \cdot t}}{(k_1 + k_2) \cdot (k_1 + k_2 - k_3 - k_4)} \cdot k_2 + \frac{k_4}{k_1 + k_2} \cdot \frac{k_2}{k_4 + k_3} + e^{[(-k_3) - k_4] \cdot t} \cdot \frac{k_3}{k_1 + k_2 - k_3 - k_4} \cdot \frac{k_2}{k_4 + k_3} \right] \cdot C_{A0} \\ \left[e^{[(-k_1) - k_2] \cdot t} \cdot \frac{k_3}{(k_1 + k_2) \cdot (k_1 + k_2 - k_3 - k_4)} \cdot k_2 + \frac{k_3}{k_1 + k_2} \cdot \frac{k_2}{k_4 + k_3} - e^{[(-k_3) - k_4] \cdot t} \cdot \frac{k_3}{k_1 + k_2 - k_3 - k_4} \cdot \frac{k_2}{k_4 + k_3} \right] \cdot C_{A0} \end{bmatrix}$$

Fig. 2.6 Calculating the vector of the substance current concentrations

very awkward and can be simplified by multiplying their separate columns by a definite constant. But a user will have to perform such simplification by himself. The versions 13 and 14, in which columns of an eigenvector matrix are displayed in a maximally simplified form, are free from this disadvantage.

All the enumerated stages of the matrix solution of an ODE system can be, of course, also realized by the Maple suits. However, provided there is the function `dsolve` which copes with linear systems without difficulty, using of the classical matrix method is unnecessary.

2.3 The Laplace Transform in Kinetic Calculations

2.3.1 Brief Notes from Operational Calculus

The *Laplace transformation* is one of central notions of *operational calculus*. The most important application of the latter is analytical seeking of general and particular solutions of some types of differential equations and systems, including ones containing partial derivatives.

In operational calculus, a function $F(s)$ determined by the equality:

$$F(s) = \int_0^{\infty} e^{-st} f(t) dt, \quad (2.4)$$

where s is a positive real number or a complex number with a positive real part, is assigned to a real function $f(t)$ determined at $t \geq 0$.¹ A function $f(t)$ is named an *original function* or *inverse transform* and $F(s)$ is a *Laplace transform*. Transfer from an original function $f(x)$ to a function $F(x)$ according to (2.4) is named the *direct* Laplace transform. Respectively, transformation of $F(x)$ in an original function is named the *inverse* Laplace transform and performed according to the formula

$$f(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{st} F(s) ds. \quad (2.5)$$

The method of solving linear differential equations and systems using the Laplace transform is named *operational*. The point of the method is that functions and their derivatives entering differential equations (original functions) are transformed into

¹The restriction $t \geq 0$ does not imply by any means automatic restriction of a class of problems which can be solved using the Laplace transform. In the vast majority of dynamic models, an independent variable t is time. System behaviour at “negative” time values makes no difference to us.

Laplace transforms according to formula (2.4). As a result of such transform, source differential equations of original functions are represented in an operational form. It is quite important that an algebraic equation of Laplace transforms corresponds to a separate linear differential equation of original functions. In fact, the Laplace transform allows to replace the operation of differentiating with multiplication. Next, an analytical solution of a modified equation (an operator solution) is sought and subjected to the inverse Laplace transform, with definite rules being followed (formula (2.5)), thus yielding a solution of a source differential equation or an ODE system.

In the “precomputer” age the above-stated sequence of operations was performed, as a rule, using special tables of original functions and Laplace transforms. Modern mathematical packages, including Mathcad and Maple, are equipped with corresponding tools to perform the direct and inverse Laplace transforms.

In the Mathcad environment, the direct Laplace transform of an original function is taken using either the command menu `Symbolics|Transform|Laplace` or the symbolic editor panel. An argument name is obligatorily indicated after calling the keyword `laplace`. When the inverse transform is being performed, the menu entry `Symbolics|Transform|InverseLaplace` or the operator `invlaplace` in the symbolic commands pallet can be used. In the last case a name of a Laplace transform is indicated. An example of performing the stated operations is given in Fig. 2.7.

$$\begin{array}{ll}
 e^t \text{ laplace, } t \rightarrow \frac{1}{s-1} & \frac{1}{s-1} \text{ invlaplace, } s \rightarrow e^t \\
 e^{a \cdot t} \text{ laplace, } t \rightarrow \frac{1}{s-a} & \frac{1}{s-a} \text{ invlaplace, } s \rightarrow e^{a \cdot t} \\
 \text{Homogeneity property} & k \cdot f_1(t) \text{ laplace, } t \rightarrow k \cdot \text{laplace}\{f_1(t), t, s\} \\
 \sin(t) \text{ laplace, } t \rightarrow \frac{1}{s^2+1} & 2 \cdot \sin(t) \text{ laplace, } t \rightarrow \frac{2}{s^2+1} \\
 f_1(t) \text{ laplace, } t \rightarrow \text{laplace}\{f_1(t), t, s\} & f_2(t) \text{ laplace, } t \rightarrow \text{laplace}\{f_2(t), t, s\} \\
 \text{Linear property} & f_1(t) + f_2(t) \text{ laplace, } t \rightarrow \text{laplace}\{f_1(t), t, s\} + \text{laplace}\{f_2(t), t, s\} \\
 e^t + e^{b \cdot t} \text{ laplace, } t \rightarrow \frac{1}{s-1} + \frac{1}{s-b} \\
 \text{Original differentiation} & \\
 \frac{d}{dt} f(t) \text{ laplace, } t \rightarrow s \cdot \text{laplace}\{f(t), t, s\} - f(0) & \\
 \frac{d^2}{dt^2} f(t) \text{ laplace, } t \rightarrow s \cdot (s \cdot \text{laplace}\{f(t), t, s\} - f(0)) - \left. \frac{d}{dt} f(t) \right|_{t \leftarrow 0} &
 \end{array}$$

Fig. 2.7 The Laplace transformation in Mathcad

$$\begin{aligned}
\frac{d}{dt}C_B(t) &= k_1 \cdot C_{A0} \cdot \exp\{-k_1 \cdot t\} - k_2 \cdot C_B(t) & B(0) &= 0 \\
\frac{d}{dt}C_B(t) \text{ laplace, } t &\rightarrow s \cdot \text{laplace}\{C_B(t), t, s\} - C_B(0) \\
k_1 \cdot C_{A0} \cdot \exp\{-k_1 \cdot t\} - k_2 \cdot C_B(t) \text{ laplace, } t &\rightarrow k_1 \cdot \frac{C_{A0}}{s + k_1} - k_2 \cdot \text{laplace}\{C_B(t), t, s\} \\
s \cdot LB &= k_1 \cdot \frac{C_{A0}}{s + k_1} - k_2 \cdot LB \text{ solve, } LB \rightarrow k_1 \cdot \frac{C_{A0}}{(s + k_1) \cdot (s + k_2)} \\
k_1 \cdot \frac{C_{A0}}{(s + k_1) \cdot (s + k_2)} \text{ invlaplace, } s &\rightarrow k_1 \cdot C_{A0} \cdot \left[\frac{-1}{k_1 - k_2} \cdot e^{(-k_1) \cdot t} + \frac{1}{k_1 - k_2} \cdot e^{(-k_2) \cdot t} \right]
\end{aligned}$$

Fig. 2.8 Applying the operator method to derivation of the kinetic curve equation for the intermediate of the consecutive reaction

To learn only the most important rules of operational calculus related to properties of original functions and Laplace transforms is enough to successfully solve many kinetic problems. These properties are following:

- *Homogeneity property.* If a Laplace transform $F(s)$ corresponds to a function $f(t)$, then at a given real or complex constant k a Laplace transform $kF(s)$ corresponds to a function $kf(t)$;
- *Linear property.* A linear combination of Laplace transforms corresponds to a linear combination of original functions.

These simple rules are illustrated in Fig. 2.7.² The examples of applying the Laplace transform to the derivatives of the original functions are also represented here. As one can see, the transform is reduced to replacement of the differentiation operator with the factor containing the argument s . In addition, the expression of the Laplace transform contains the values of the function and its derivatives at a zero point $x(0)$, $x'(0)$, $\dots$ $x^{(n)}(0)$, i.e. the initial conditions for the source differential equation.³

Let us consider an example of using the operator method for solving a differential equation describing a concentration change of an intermediate during a first-order consecutive reaction (Fig. 2.8). The original function here is the intermediate current concentration $C_B(t)$. A use of the Mathcad operator `laplace` leads to the Laplace transform of this function in the form `laplace( $C_B(t)$ ,  $t$ ,  $s$ )`. Pay attention to the result of the transform of the derivative $C_B'(t)$. Besides the

²Many of the documents represented in this chapter do not work in Mathcad 14. While embedding the symbolic kernel MuPAD, developers did not notice that the command `laplace` do not carry out its tasks to the full extent. By the time this book is published, this mistake might be already corrected.

³Instead of initial conditions, arbitrary constants $C_1, C_2, \dots, C_n$ can be specified. Then it is obvious that the operator method is also applicable to seeking a general solution of an equation.

Laplace transform, it also contains the value of $C_B(0)$, *i.e.* the initial condition for solving the problem. After that, the form `laplace(CB(t), t, s)` is replaced with the variable `LB` and the resulting algebraic equation is solved for this variable. Next, the operator solution is subjected to the inverse Laplace transform (the operator `invlaplace, s`). The final expression defines the analytical form of the function $C_B(t)$.

The same sequence of the operations can be performed by the Maple suites. But in contrast to Mathcad, where a user has to find a Laplace transform and recover an original function himself, the Maple's operator method for solving an ODE is almost completely automated. If it is necessary to find a solution by means of mathematical apparatus of operational calculus, it is enough to specify an additional option in the body of `dsolve` in the form of the expression `method = laplace`. Let us illustrate this for seeking the general solution of the linear second-order differential equation

$$y(x) = a + \frac{d^2y(x)}{dx^2},$$

in Maple.

At first sight, this equation seems to be too abstract and not related to chemical kinetics. However, we will need it in the below problems. Thus, we will show below (Chap. 5) that more complicated relationships describing, in particular, diffusion and heat transfer processes can be reduced to an equation of this type.

In the Maple document given in Fig. 2.9 the considered equation is solved twice. First, `dsolve` uses "classical" built-in suits for seeking an analytical solution by default, and then the same equation is solved by means of the Laplace transform (the option `method = laplace`). In addition, the document uses some other functions. Thus, the command `odeadvisor` diagnoses the differential equation and ascertains which type of equations it belongs to. In the both cases, the function `infolevel[dsolve]` helps to observe the process of solving. The both functions enter the command library `DEtools`. To link the library of functions and commands of integral transforms (`inttrans`) is necessary to implement the operator method. Though the form of visualization of the final result is different in the each case, checking the solution `Sol` of the equation `eq` with the help of the command `odetest(Sol, eq)` shows that the both forms are equivalent.

2.3.2 Derivation of Kinetic Equations for Linear Sequences of First-Order Reactions

For this type of reactions, ideology of the operator method in respect to solving systems of linear differential equations remains completely the same but in this case, when applying the Laplace transform, we obtain not a separate algebraic

```

[> restart;with(DEtools):
> eq:=y(x)=a+diff(y(x),x$2);


$$eq = y(x) = a + \left( \frac{d^2}{dx^2} y(x) \right)$$


> odeadvisor(eq);

[[_2nd_order,_missing_x]]
> infolevel[dsolve]:=2:s1:=dsolve(eq,y(x));
Methods for second order ODEs:
--- Trying classification methods ---
trying a quadrature
trying high order exact linear fully integrable
trying differential order: 2; linear nonhomogeneous with symmet
ry [0,1]
trying a double symmetry of the form [xi=0, eta=F(x)]
Try solving first the homogeneous part of the ODE
checking if the LODE has constant coefficients
<- constant coefficients successful
<- solving first the homogeneous part of the ODE successful


$$s1 = y(x) = e^{(-x)}\_C2 + e^x\_C1 + a$$


> with(inttrans):s2:=dsolve(eq,y(x),method=laplace
);
dsolve/inttrans/solveit: Transform of eqns is ('laplace/int
ernal'(y(x),x,_s1)-a/_s1-_s1^2*'laplace/internal'(y(x),x,_s1)+D
(y)(0)+_s1*y(0))
dsolve/inttrans/solveit: Algebraic Solution is ('laplace/in
ternal'(y(x),x,_s1) = (-a+D(y)(0)*_s1+_s1^2*y(0))/_s1/(-1+_s1^2
))


$$s2 = y(x) = a + (-a + y(0)) \cosh(x) + D(y)(0) \sinh(x)$$


> odetest(s2,eq);
0

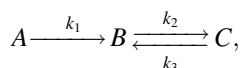
> odetest(s1,eq);
0

```

Fig. 2.9 The operator method in Maple

equation but a system of linear equations which can be solved either by `lsolve` or using the solving block `GIVEN/FIND`.

Thus, Fig. 2.10 represents the Mathcad document meant for solving the ODE system using by the operator method. The system describes kinetics of the first-order consecutive reaction with the reversible second step



at the initial concentration of the source reactant C_{A_0} . The Laplace transform is applied here to the each equation of the source system and then the system of the algebraic equations is formed of the obtained Laplace transforms. Next, its operator solution is subjected to the inverse Laplace transform.

Note that an operator solution of an equation system using the symbolic Mathcad suits is always represented as a vector. The symbolic command `invlaplace`

$$\begin{array}{c}
 \boxed{A \xrightarrow{k_1} B \xrightleftharpoons[k_3]{k_2} C} \quad \begin{array}{l} \frac{d}{dt} C_A(t) = -k_1 \cdot C_A(t) \quad \frac{d}{dt} C_B(t) = k_1 \cdot C_A(t) - k_2 \cdot C_B(t) + k_3 \cdot C_C(t) \\ C_A(0) = C_{A0} \quad C_B(0) = 0 \quad \frac{d}{dt} C_C(t) = k_2 \cdot C_B(t) - k_3 \cdot C_C(t) \quad C_C(0) = 0 \end{array} \\
 \\
 \begin{array}{l} \frac{d}{dt} C_A(t) + k_1 \cdot C_A(t) \quad \left| \begin{array}{l} \text{laplace, } t \\ \text{substitute, } C_A(0) = C_{A0} \end{array} \right. \rightarrow s \cdot \text{laplace}\{C_A(t), t, s\} - C_{A0} + k_1 \cdot \text{laplace}\{C_A(t), t, s\} \\ \frac{d}{dt} C_B(t) - \{k_1 \cdot C_A(t) - k_2 \cdot C_B(t) + k_3 \cdot C_C(t)\} \quad \text{laplace, } t \rightarrow \\ \rightarrow s \cdot \text{laplace}\{C_B(t), t, s\} - C_B(0) - k_1 \cdot \text{laplace}\{C_A(t), t, s\} + k_2 \cdot \text{laplace}\{C_B(t), t, s\} - k_3 \cdot \text{laplace}\{C_C(t), t, s\} \\ \frac{d}{dt} C_C(t) - \{k_2 \cdot C_B(t) - k_3 \cdot C_C(t)\} \quad \text{laplace, } t \rightarrow s \cdot \text{laplace}\{C_C(t), t, s\} - C_C(0) - k_2 \cdot \text{laplace}\{C_B(t), t, s\} + k_3 \cdot \text{laplace}\{C_C(t), t, s\} \end{array} \\
 \\
 \text{Given} \quad s \cdot LA - C_{A0} + k_1 \cdot LA = 0 \quad s \cdot LB - k_1 \cdot LA + k_2 \cdot LB - k_3 \cdot LC = 0 \quad s \cdot LC - k_2 \cdot LB + k_3 \cdot LC = 0 \\
 \\
 \text{Find}(LA, LB, LC) \text{ collect, } s \rightarrow \left[\begin{array}{c} \frac{C_{A0}}{s + k_1} \\ \frac{C_{A0}}{s \cdot [s^2 + (k_2 + k_1 + k_3) \cdot s + k_2 \cdot k_1 + k_3 \cdot k_1]} \cdot (s + k_3) \\ \frac{k_1 \cdot C_{A0}}{s \cdot [s^2 + (k_2 + k_1 + k_3) \cdot s + k_2 \cdot k_1 + k_3 \cdot k_1]} \end{array} \right] \\
 \\
 \frac{C_{A0}}{s + k_1} \text{ invlaplace, } s \rightarrow C_{A0} \cdot e^{(-k_1) \cdot t} \quad \boxed{\gamma_1 + \gamma_2 = k_2 + k_1 + k_3} \quad \boxed{\gamma_1 \cdot \gamma_2 = k_2 \cdot k_1 + k_3 \cdot k_1} \\
 \\
 \begin{array}{l} \frac{C_{A0}}{s \cdot [s^2 + (\gamma_1 + \gamma_2) \cdot s + \gamma_1 \cdot \gamma_2]} \cdot (s + k_3) \quad \left| \begin{array}{l} \text{invlaplace, } s \\ \text{collect, } e^{(-\gamma_2) \cdot t} \rightarrow \left[\frac{1}{\gamma_1 \cdot (\gamma_1 - \gamma_2)} \cdot k_3 - \frac{1}{\gamma_1 - \gamma_2} \right] \cdot e^{(-\gamma_1) \cdot t} \\ \text{collect, } e^{(-\gamma_1) \cdot t} \\ \text{collect, } k_1 \cdot C_{A0} + \left[\frac{-1}{\gamma_2 \cdot (\gamma_1 - \gamma_2)} \cdot k_3 + \frac{1}{\gamma_1 - \gamma_2} \right] \cdot e^{(-\gamma_2) \cdot t} + \frac{k_3}{\gamma_1 \cdot \gamma_2} \end{array} \right. \\ \left. C_{A0} \cdot k_1 \right] \\
 \\
 \frac{k_2}{s \cdot [s^2 + (\gamma_1 + \gamma_2) \cdot s + \gamma_1 \cdot \gamma_2]} \text{ invlaplace, } s \rightarrow k_1 \cdot C_{A0} \cdot k_2 \left[\frac{1}{\gamma_1 \cdot \gamma_2} - \frac{1}{\gamma_2 \cdot (\gamma_1 - \gamma_2)} \cdot e^{(-\gamma_2) \cdot t} + \frac{1}{\gamma_1 \cdot (\gamma_1 - \gamma_2)} \cdot e^{(-\gamma_1) \cdot t} \right] \end{array}
 \end{array}$$

Fig. 2.10 Solving the system of the linear differential equations by means of the operator method

cannot be applied to a whole vector on the stage of subsequent transfer to original functions. Each vector element should be treated separately.

Certain inconveniencies of realization of the operator method in Mathcad are connected with an order of display of symbolic results adopted in this package. When recovering original functions corresponding to found Laplace transforms, a user often has to deal with very awkward expressions displayed in one line and using symbolic commands like `simplify` or `collect` does not enable to represent a result in a more compact form. Here, introducing new parameters equal to some combinations of rate constants can help significantly. Thus, for the purpose of obtaining more compact expressions, the operator solution in Fig. 2.10 is somehow modified by introducing the new constants γ_1 and γ_2 satisfying the equalities

$$\gamma_1 + \gamma_2 = k_1 + k_2 + k_3; \quad \gamma_1 \gamma_2 = k_1(k_2 + k_3).$$

The kinetic curves of the substances taking part in the reaction plotted in Fig. 2.11 reveal a significant difference from the analogous dependencies for the

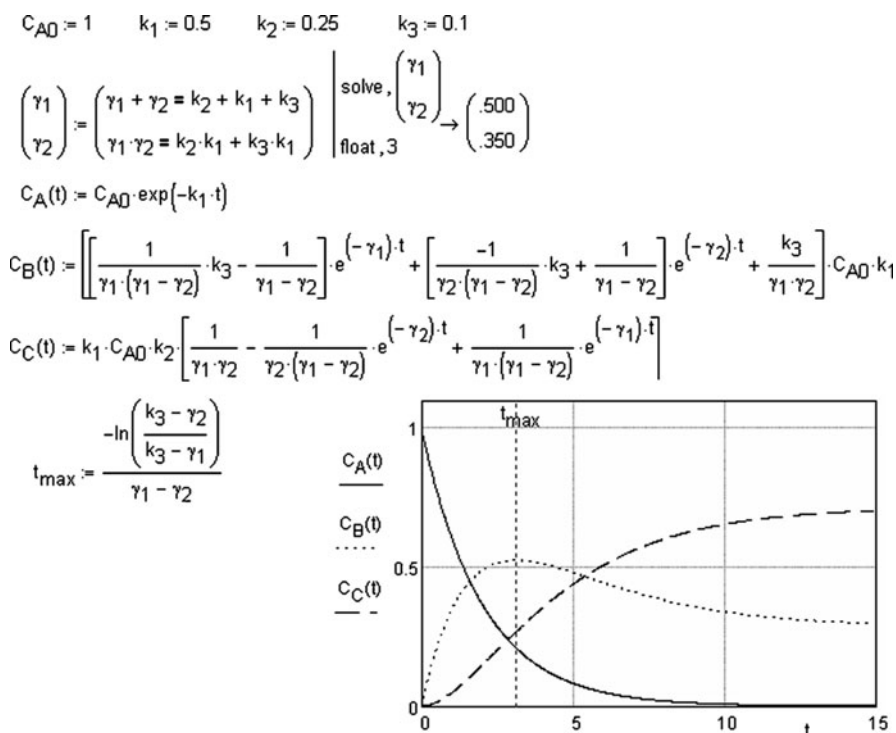


Fig. 2.11 Kinetics of the two-step first-order consecutive reaction with the reversible second step

irreversible consecutive reaction. This difference consists in stabilization of concentrations of the intermediate and the end product with time owing to establishing the equilibrium of the second and third steps.

The intermediate concentration passes through a maximum, as in the case of the irreversible consecutive reaction. Respectively, the end product curve has an inflection. However, the abscissa of the maximum point $t_{\max}$ (in this case it coincides with the abscissa of the reflection point) is now determined by a relationship of the rate constants of all the elementary stages. It is easy to make sure that:

$$t_{\max} = \frac{\ln\left(\frac{k_1 - k_3}{k_2}\right)}{k_1 - k_2 - k_3}.$$

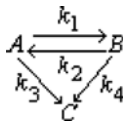
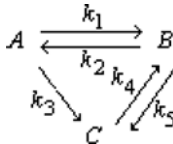
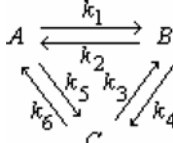
Thereby, in the symbolic commands `laplace`, `invlaplace` of the Mathcad package we have one more quite reliable instrument for solving the direct problem of chemical kinetics for multi-step reactions described by systems of linear differential equations. The examples of the kinetic equations for some reactions are represented in Table 2.1. Naturally, the classical matrix method can be used to derive these equations. In Maple, capabilities of `dsolve` are enough for this.

Table 2.1 Analytical solutions of the direct problem for some reaction systems with elementary first-order steps

Reaction schemes and initial concentrations	Kinetic curve equations
1	2
1. The irreversible consecutive reaction	
$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 e^{-k_1 t}; B(t) = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t});$ $C(t) = A_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right)$
2. The consecutive reaction with the second step being reversible	
$A \xrightarrow{k_1} B \xrightleftharpoons[k_3]{k_2} C$ $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 e^{-k_1 t}$ $B(t) = k_1 A_0 \left[\frac{k_3}{\gamma_1 \gamma_2} + \frac{\gamma_2 - k_3}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_2 t} + \frac{k_3 - \gamma_1}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} \right];$ $C(t) = k_1 k_2 A_0 \left[\frac{1}{\gamma_1 \gamma_2} + \frac{1}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} - \frac{1}{\gamma_2 (\gamma_1 - \gamma_2)} e^{-\gamma_2 t} \right];$ where $\gamma_1 \gamma_2 = k_1 (k_2 + k_3)$, $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3$
3. The consecutive reaction with the first step being reversible	
$A \xrightleftharpoons[k_2]{k_1} B \xrightarrow{k_3} C$ $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = \frac{A_0}{\gamma_2 - \gamma_1} [(k_2 + k_3 - \gamma_1) e^{-\gamma_1 t} - (k_2 + k_3 - \gamma_2) e^{-\gamma_2 t}]$ $B(t) = \frac{A_0 k_1}{\gamma_2 - \gamma_1} (e^{-\gamma_1 t} - e^{-\gamma_2 t});$ $C(t) = A_0 \left[1 + \frac{k_1 k_3}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{k_1 k_3}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right]$ where $\gamma_1 \gamma_2 = k_1 k_3$; $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3$
4. The competitive reaction with a reversible step	
$\begin{array}{c} A \xrightleftharpoons[k_2]{k_1} B \\ \downarrow k_3 \\ C \end{array}$ $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 \left(\frac{k_2 - \gamma_1}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} - \frac{k_2 - \gamma_2}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$ $B(t) = \frac{k_1 A_0}{\gamma_2 - \gamma_1} (e^{-\gamma_1 t} - e^{-\gamma_2 t});$ $C(t) = A_0 \left[1 + \frac{k_3 (k_2 - \gamma_1)}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{k_3 (k_2 - \gamma_2)}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right]$ $\gamma_1 \gamma_2 = k_2 k_3$; $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3$
5. The consecutive two-step reaction with both steps being reversible	
$A \xrightleftharpoons[k_2]{k_1} B \xrightleftharpoons[k_4]{k_3} C$ $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 \left[\frac{k_2 k_4}{\gamma_1 \gamma_2} - \frac{k_1 (\gamma_1 - k_3 - k_4)}{\gamma_1 (\gamma_2 - \gamma_1)} e^{-\gamma_1 t} - \frac{k_1 (k_3 + k_4 - \gamma_2)}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right]$ $B(t) = A_0 k_1 \left[\frac{k_4}{\gamma_1 \gamma_2} + \frac{k_4 - \gamma_1}{\gamma_1 (\gamma_2 - \gamma_1)} e^{-\gamma_1 t} + \frac{k_4 - \gamma_2}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right]$ $C(t) = A_0 k_1 k_3 \left[\frac{1}{\gamma_1 \gamma_2} + \frac{1}{\gamma_1 (\gamma_2 - \gamma_1)} e^{-\gamma_1 t} - \frac{1}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right],$ where $\gamma_1 \gamma_2 = k_2 k_4 + k_1 k_3 + k_1 k_4$; $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4$

(continued)

Table 2.1 (continued)

Reaction schemes and initial concentrations	Kinetic curve equations
6. The consecutive-competitive reaction with a reversible step	
 $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = \frac{A_0}{\gamma_2 - \gamma_1} [(k_2 + k_3 - \gamma_1)e^{-\gamma_1 t} - (k_2 + k_3 - \gamma_2)e^{-\gamma_2 t}];$ $B(t) = \frac{k_1 A_0}{\gamma_2 - \gamma_1} (e^{-\gamma_1 t} - e^{-\gamma_2 t});$ $C(t) = A_0 \left(1 - \frac{\gamma_2 - k_4}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} - \frac{\gamma_1 + k_4}{\gamma_1 - \gamma_2} e^{-\gamma_2 t} \right),$ where $\gamma_1 \gamma_2 = k_1 k_3 + k_2 k_4 + k_3 k_4;$ $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4$
7. The consecutive-competitive reaction with two steps being reversible	
 $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 \left(\frac{k_2 k_5}{\gamma_1 \gamma_2} - \frac{\gamma_2^2 - \varepsilon \gamma_2 + k_2 k_5}{\gamma_2 (\gamma_1 - \gamma_2)} e^{-\gamma_2 t} - \frac{\gamma_1^2 - \varepsilon \gamma_1 + k_2 k_5}{\gamma_1 (\gamma_2 - \gamma_1)} e^{-\gamma_1 t} \right)$ $B(t) = A_0 \left(\frac{\eta}{\gamma_1 \gamma_2} - \frac{k_1 \gamma_2 - \eta}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} - \frac{k_1 \gamma_1 - \eta}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} \right);$ $C(t) = A_0 \left(\frac{\delta}{\gamma_1 \gamma_2} - \frac{k_3 \gamma_2 - \delta}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} - \frac{k_3 \gamma_1 - \delta}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} \right);$ где $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4 + k_5;$ $\gamma_1 \gamma_2 = k_2 k_3 + k_1 k_4 + k_2 k_5 + k_3 k_5 + k_3 k_4 + k_1 k_5;$ $\delta = \gamma_1 \gamma_2 - k_2 k_5 - k_3 k_5 - k_1 k_5;$ $\eta = \gamma_1 \gamma_2 - k_2 k_3 - k_1 k_4 - k_2 k_5 - k_3 k_4;$ $\varepsilon = \gamma_1 + \gamma_2 - k_1 - k_3$
8. The consecutive two-step reaction with three steps being reversible	
 $A(0) = A_0; B(0) = 0;$ $C(0) = 0$	$A(t) = A_0 \left(\frac{\beta}{\gamma_1 \gamma_2} + \frac{\alpha \gamma_1 - \gamma_1^2 - \beta}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\gamma_2^2 - \alpha \gamma_2 + \beta}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$ $B(t) = A_0 \left(\frac{\varepsilon}{\gamma_1 \gamma_2} + \frac{k_1 \gamma_1 - \varepsilon}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\varepsilon - k_1 \gamma_2}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$ $C(t) = A_0 \left(\frac{\delta}{\gamma_1 \gamma_2} + \frac{k_5 \gamma_1 - \delta}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\delta - k_5 \gamma_2}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right),$ where $\alpha = k_2 + k_3 + k_4 + k_6; \beta = k_2 k_4 + k_2 k_6 + k_3 k_6;$ $\varepsilon = k_1 k_4 + k_1 k_6 + k_4 k_5; \delta = k_1 k_3 + k_2 k_5 + k_3 k_5;$ $\gamma_1 \gamma_2 = \beta + \varepsilon + \delta; \gamma_1 + \gamma_2 = \alpha + k_1 + k_5$

2.3.3 Transient Regime in a System of Flow Reactors

Heretofore, the kinetic models of the reactions proceeding in closed systems have been considered. In such systems material exchange with surroundings is excluded (batch reactors). In practice, many reactions are carried out in open systems under a regime of continuous feed of reactants to a reactor and withdrawal of formed

products from it. There are two continuous reactor models: a *batch* reactor and a *plug flow* one.

Let us consider a stirred tank reactor (STR). In such reactor, a reaction mixture is stirred in the way that current concentrations of reactants taking part in a reaction are the same at any time moment in any point of reaction space. Let the first-order reaction $A \xrightarrow{k} B$ proceed in the STR. The solution of reactant A with a concentration of C_0 is continuously fed to the reactor inlet with a rate of $v \text{ l s}^{-1}$. The reaction mixture is withdrawn from the reactor with the same rate. Under these conditions, the reaction space volume remains constant and is V . The change of the reactant quantity per unit of time is:

$$\frac{dn_A(t)}{dt} = vC_0 - vC_A(t) - kC_A(t)V. \quad (2.6)$$

Dividing the both parts of the equation by V yields the mathematical model of the STR in the form:

$$\frac{dC_A(t)}{dt} = -kC_A(t) + \frac{v}{V}(C_0 - C_A(t)). \quad (2.7)$$

Thus, in contrast to the kinetic equation describing the first-order reaction in a batch reactor, the last equation contains the summand which characterizes geometrical dimensions of the reactor and the rate of substance feed to the reactor and its withdrawal from it.

Solving (2.8) at the initial reactant concentration (Fig. 2.12) shows that the current reactant concentration depends on the kinetic and macroscopic parameters of the system in a complicated way,

$$C_A(t) = \frac{C_{A_0}}{kV + v} \left[v + kV e^{-(k+\frac{v}{V})t} \right].$$

The graph zone represented in Fig. 2.12 shows that the kinetic curve of the source reactant has a characteristic feature: in the course of time the concentration becomes time-constant. We met the similar curve behaviour when analyzing reversible reactions; however, in this case, stabilization of the concentration with time is not related to establishing the chemical equilibrium state. In the case under consideration, we have a *steady-state regime* of the process, a state when a reactant loss because of proceeding a reaction is precisely compensated by its gain at the expense of feed of new reactant portions to a reactor. The expression for the steady-state concentration of substance A is easily reduced by equating the derivative in (2.7) to zero

$$C_{A_{st}} = C_{A_0} \frac{v}{kV + v}.$$

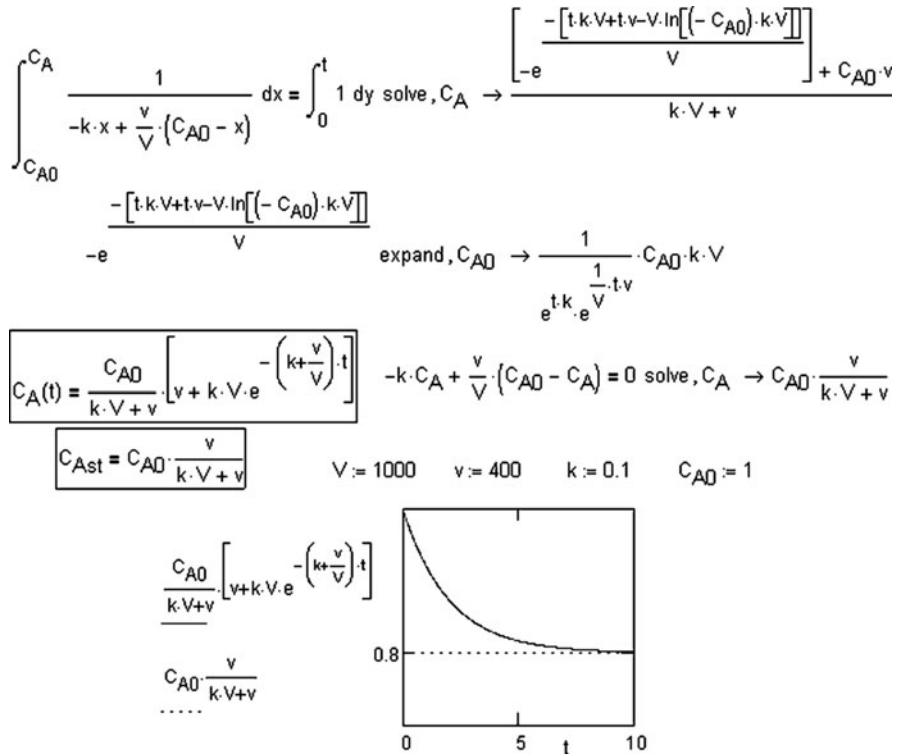


Fig. 2.12 The time dependence of the reactant concentration in the stirred tank reactor

Let us now consider a cascade of three stirred tank reactors of volumes of V_1 , V_2 , V_3 and with current concentrations of C_1 , C_2 , C_3 , respectively. The scheme of the reaction mixture flows for the each reactor is represented in Fig. 2.13.

The first reactor has two inlets, vC_0 mol s^{-1} of reactant A are fed to the first one from the outside and v_1C_2 mol s^{-1} enter the second one from reactor 2. For substance A, the outlet matter flow of reactor 1 and the inlet matter flow of reactor 2 are equal to $(v + v_1)C_1$ mol s^{-1} . The outlet matter flow of reactor 2 is $(v + v_1)C_2$ mol s^{-1} and next is divided between two paths. Its part v_1C_2 mol s^{-1} returns into reactor 1 and vC_2 mol s^{-1} is fed to the inlet of reactor 3. vC_3 mol L^{-1} of substance A is eventually withdrawn from the system. In connection with the above and taking into account relationships (2.6) and (2.7), we can write the equations describing the time-dependent loss of the reactant concentration in the each reactor

$$dn_1(t)/dt = vC_0 + v_1C_2(t) - (v + v_1)C_1(t) - kC_1(t)V_1,$$

$$dn_2(t)/dt = (v + v_1)C_1(t) - (v + v_1)C_2(t) - kC_2(t)V_2,$$

$$dn_3(t)/dt = vC_2(t) - vC_3(t) - kC_3(t)V_3,$$

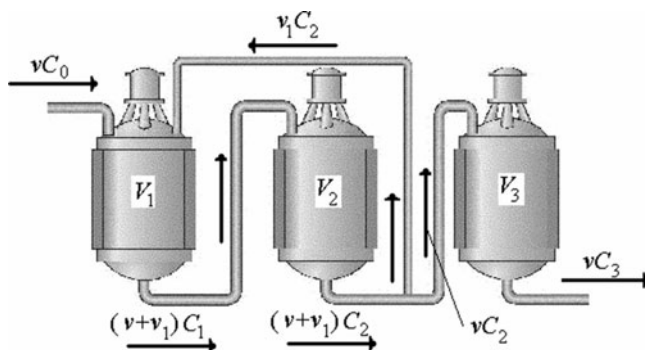


Fig. 2.13 The cascade of the stirred tank reactors

or

$$\frac{dC_1(t)}{dt} = -kC_1(t) + \frac{vC_0 + v_1C_2(t) - (v + v_1)C_1(t)}{V_1},$$

$$\frac{dC_2(t)}{dt} = -kC_2(t) + \frac{(v + v_1)[C_1(t) - C_2(t)]}{V_2},$$

$$\frac{dC_3(t)}{dt} = -kC_3(t) + \frac{v[C_2(t) - C_3(t)]}{V_3}.$$

The obtained system of the linear differential equations can be solved by applying the operational system apparatus.

Let us consider that before starting the reaction, the concentrations of A in the each reactor are the same and equal to $C_0 \text{ mol L}^{-1}$. Additionally, let us intentionally complicate the conditions of the direct kinetic problem. Assume that in the each reactor the reaction mixture has different temperature and this temperature remains constant during the process (here, of course, we have to assume that new portions of the solution immediately takes a given reactor temperature). Thus, this means that the process is controlled by the different rate constants k_1, k_2, k_3 in the each reactor.

Figure 2.14 represents the part of the network variant of the Mathcad document which allows to model different situations of a system behaviour at different values of the input parameters, namely the rate constants k_1, k_2, k_3 , the reactor volumes V_1, V_2, V_3 , and the feed rates of the reaction mixture v, v_1 . So as not to clutter the document, constructions containing the Laplace transform are hidden from a user (this approach completely corresponds to the sequence of operations shown in Fig. 2.10). Only the elements of the vector of the operator solution as well as recovering the source original functions corresponding to the Laplace transforms are displayed in the workspace. The final result of the document is analytical expressions for the concentration–time relationships for the each reactor as well as the time dependencies of the degree of conversion of the source reactant in the

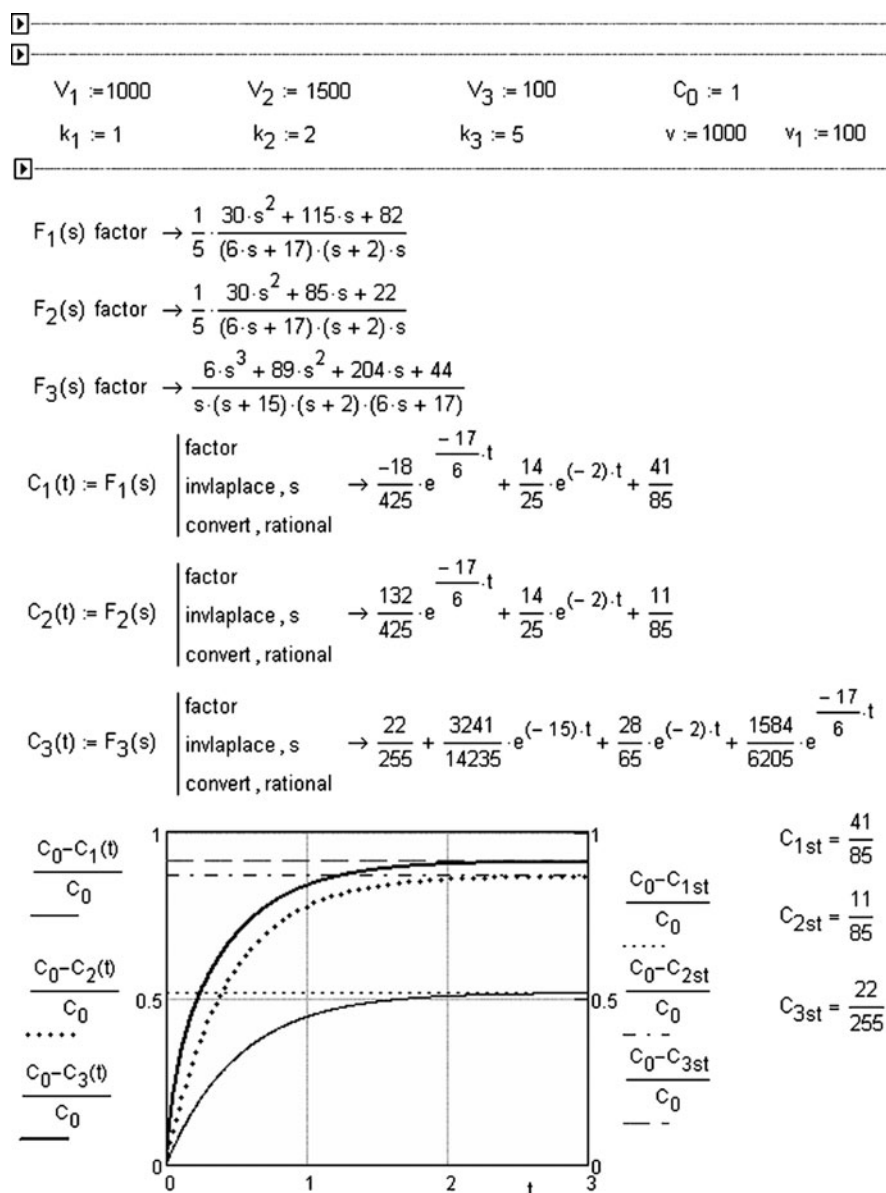


Fig. 2.14 Modeling the transient regime in the system of three reactors

each reactor. Thereby, a user has an opportunity to observe how a change of one input parameter of another influences the degree of conversion and the time of establishing a steady-state regime of operation of the reactors.

Since symbolic calculations occupy a significant part of the document, we should recommend displaying numerical values in a rational form but not as floating point

numbers for obtaining more compact expressions. Otherwise, too long expressions may be yielded what creates definite problems when printing a document. Finally, the symbolic command `convert, rational`, which transforms an expression in a rational form, can be used as shown in Fig. 2.14. Although, the last procedure is not documented and can be used only in the Mathcad versions which use the Maple symbolic kernel.

2.3.4 Kinetic Models in the Form of Equations Containing Piecewise Continuous Functions

Unfortunately, in many cases, the Mathcad symbolic processor cannot operate with functions determined using a program block. For example, an attempt to apply `laplace` to a piecewise continuous function which has been defined using the programming operators `if` and `otherwise` fails (Fig. 2.15). Meanwhile, such functions can enter differential equations describing applying different kinds of disturbances to a system under investigation (e.g., a sharp change of reactant feed to a reactor inlet, a random or intentional change of thermal conditions of a reactor, periodical injections of a medicine into an organism etc.). A head-on attempt of applying the Laplace transform to such an expression remains unsuccessful, therefore modification of the expression using the *Heaviside* function is an effective method. If a task consists in analytical solving a problem, a source piecewise continuous function should be replaced with a linear combination of other functions, with the Heaviside function $\Phi(t)$ obviously entering each summand of a new compound function. This function vanishes at negative t values and is equal to unity otherwise. Thus, Fig. 2.15 demonstrates a method of such transfer. The source function $f_1(\tau)$ is replaced with the equivalent function $f_2(\tau)$ but a distinctive feature of this new function is that symbolic commands can already be applied to it, including the command of the integral Laplace transform.

Let us consider a real problem of solving an equation with a piecewise continuous function. Suppose that substance A with the initial concentration 1 mol l^{-1} converts into the end product B during a chemical reaction, with reactant B being unstable and decomposing by the action of light to give the source substance A . If the reaction is carried out in the dark, it proceeds without any complication and the rate of decomposition of A is proportional to its current concentration. But if to expose the reaction mixture to light, the system behaviour becomes more complicated: decomposition of A is complicated by its accumulation at the expense of proceeding the reverse process whose kinetic behaviour is determined by a light intensity.

Suppose that the reaction occurs in the dark during 0.5 min and next the system is exposed to a light flux for 1.5 min. Then a light flux intensity is decreased by 75% and maintained constant. The mathematical model of the overall process can be then written in the differential equation form

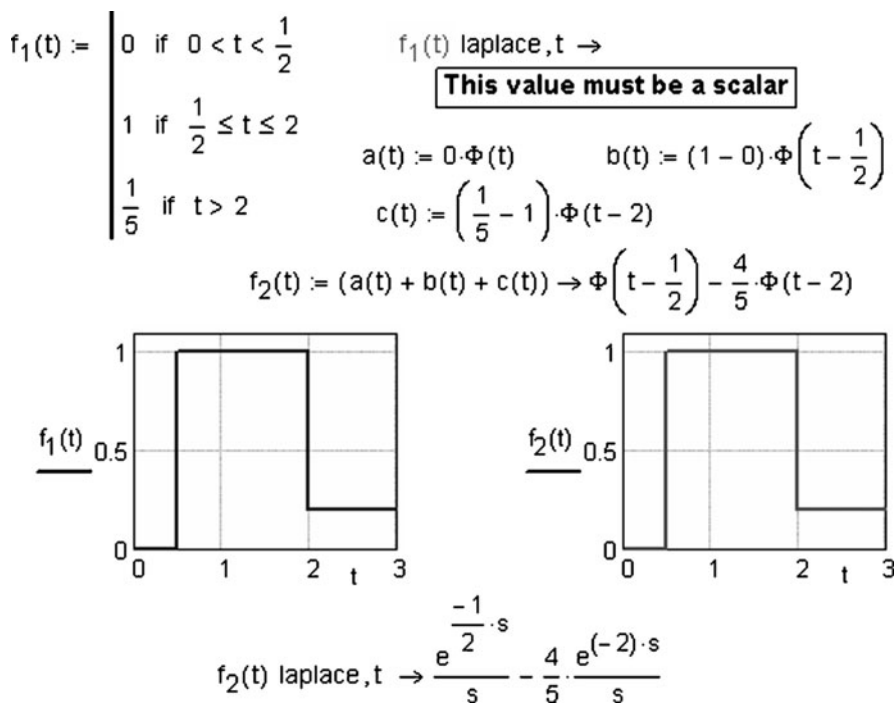


Fig. 2.15 Replacing the source function with the linear combination of the functions

$$\frac{dC_A(t)}{dt} = -kC_A(t) + f(t),$$

where the function $f(t)$ is defined by specifying the expression

$$f(t) = \Phi\left(t - \frac{1}{2}\right) + \frac{4}{5}\Phi(t - 2).$$

This problem is solved in Fig. 2.16. As we can see, the behaviour of the kinetic curve is quite complicated, however it is possible to obtain its analytical form in this case.

2.4 Approximate Methods of Chemical Kinetics

2.4.1 The Steady-State Concentration Method

Using of approximate methods of chemical kinetics is intended for, first of all, simplifying mathematical models and, respectively, their analysis. The steady-state

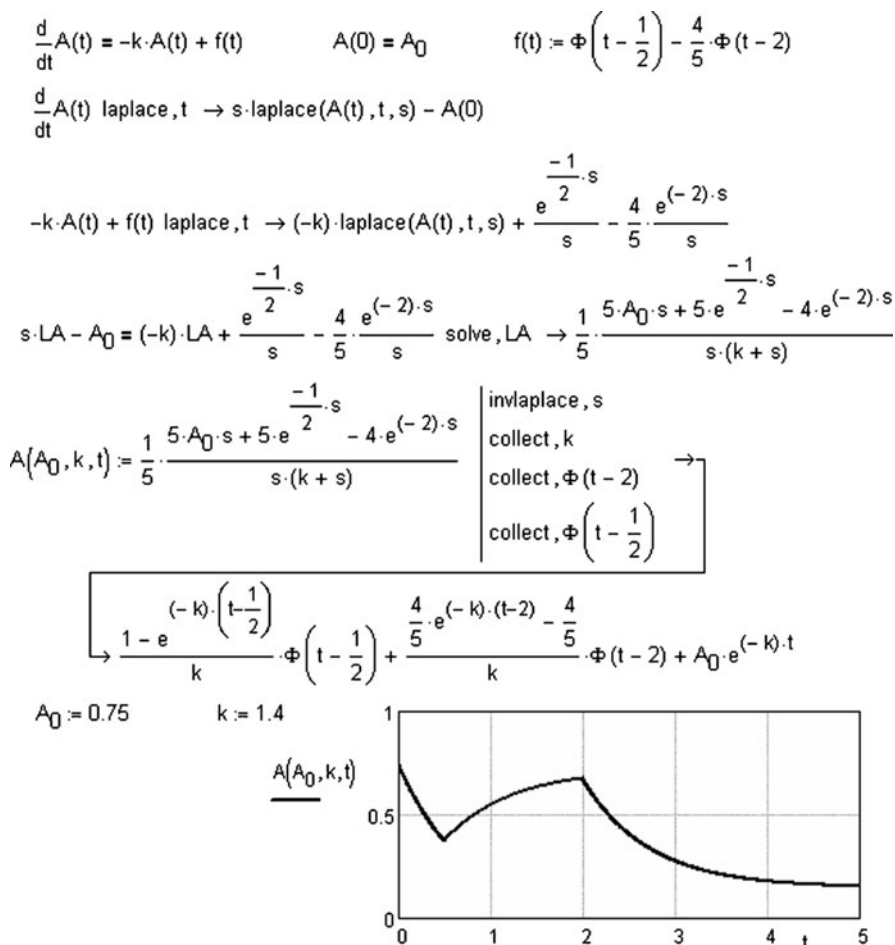


Fig. 2.16 Solving the direct problem for the reaction complicated by the photochemical conversion

concentration method is one of the most widespread approximations. This method is applicable to describing multi-step reactions whose definite steps result in high-reactivity intermediates. The condition of applying the method is a short life time of intermediates compared to a time during which reaction mixture composition can change noticeably (the *Christiansen* condition). It is assumed that time derivatives of concentrations of active intermediates are equal to zero (the *Bodenstein* theorem). Thereby, some differential equations of a system entering a mathematical model can be replaced with algebraic ones. A kinetic analysis of a reaction mechanism is considerably simplified in this case.

Let us consider a simple example to illustrate the point of the method. Let us have the kinetic scheme of the consecutive reaction with the first step being reversible



If to assume that the constant $k_3 \gg k_1$, the rate of intermediate consumption is much higher than one of its formation. Substance B is an unstable intermediate, therefore the principle of steady-state concentrations is applicable to it. Then we obtain

$$dC_B(t)/dt = k_1 C_A(t) - k_2 C_B(t) - k_3 C_B(t) = 0,$$

hence

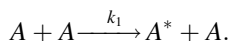
$$C_B(t) = \frac{k_1}{k_2 + k_3} C_A(t).$$

It is easy to see that the rate of product C formation is then written in the form

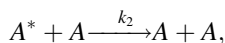
$$r_P = \frac{k_1 k_3}{k_2 + k_3} C_A(t). \quad (2.9)$$

Let us carry out a check of the steady-state principle. For this purpose, let us calculate the time dependence of the end product formation rate from the relationships obtained by accurate solving the direct kinetic problem (see Table 2.1). Next, let us compare the result with the calculations from obtained formula (2.9). The corresponding plots represented in Fig. 2.17 show that the behaviour of the both curves coincide after less than 0.5 s at given values of the rate constants satisfying the condition $k_3 \gg k_1$. This indicates applicability of the steady-state concentration method to the considered model of the consecutive reaction.

The steady-state concentration method played an important role in establishing fundamental relationships of chemical kinetics. Earlier, it was noticed that a number of monomolecular reactions involving gases have different orders with respect to a source substance depending on a gas mixture pressure. *Lindemann* assumed that the overall process of conversion of reactant A into end product P consists of a number of steps, the first one being a bimolecular collision of A molecules. Although this step does not result in a chemical conversion, it is accompanied by redistribution of colliding molecule energy and leads to formation of excited particles A^* potentially capable to overcome an energy barrier



This step is also called *excitation*. Excited molecules A^* may either loose their energy if colliding with nonexcited molecules (*deexcitation*)



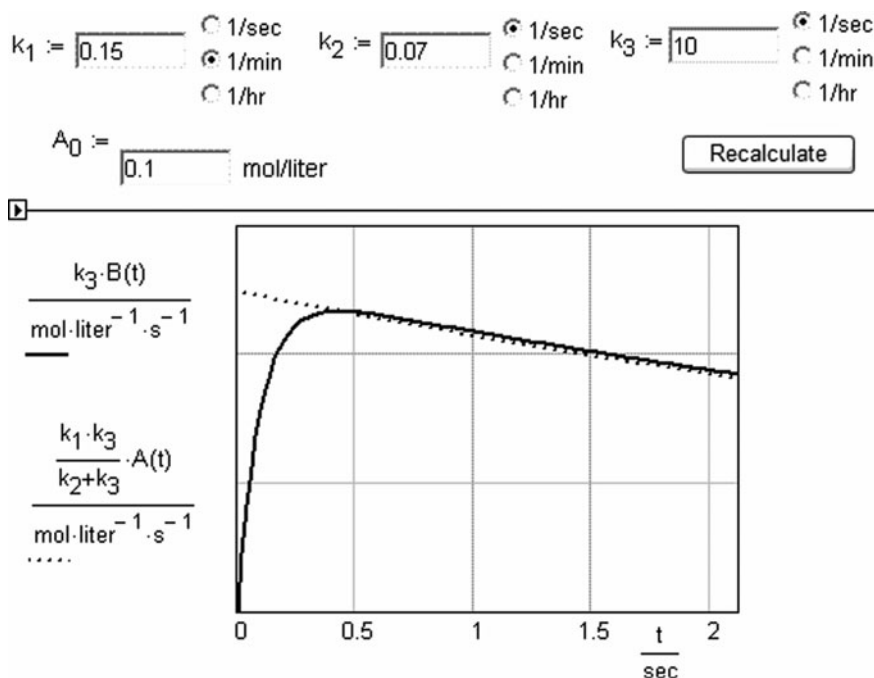
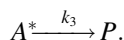


Fig. 2.17 Checking applicability of the steady-state concentration method

or be converted into the end product



Thereby, if particle A^* is considered as an unstable intermediate, the Lindemann's kinetic scheme can be analyzed in the steady-state approximation assuming $dA^*/dt \approx 0$. The results of this analysis are represented in Fig. 2.18.

In Fig. 2.18, the intermediate concentration is expressed in terms of the concentration of nonexcited molecules A and substituted into the equation for the rate r_P of the third step leading to the end product. The analysis of the obtained expression indicates two limiting cases. In the first one (a low pressure), the current concentrations (or the partial pressures) of A are so small that the term k_2A in the denominator of the expression for r_P can be neglected owing to meeting the condition $k_2A \ll k_3$. This suggests that product formation should obey relationships for a reaction having an order of 2. If transferring to a high pressure, on the contrary, $k_2A \gg k_3$. If neglecting a k_3 value, it should be concluded that we have a kinetic order of 2 for these conditions. The drawn conclusions also have a physical interpretation. Under conditions of a low pressure, molecules are too far from each other that makes the deexcitation step unlikely and the limiting step of the process is the excitation step. If transferring to a high pressure, the nature of a limiting step changes. The process rate is now determined by the third step, since wasting energy of excited particles is

$$\frac{d}{dt} A(t) = \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix}^T \cdot \begin{pmatrix} k_1 \cdot A^2 \\ k_2 \cdot A \cdot A \\ k_3 \cdot A \end{pmatrix} \left| \begin{array}{l} \text{substitute, } \frac{d}{dt} A(t) = 0 \\ \text{solve, } A \end{array} \right. \rightarrow k_1 \cdot \frac{A^2}{k_2 \cdot A + k_3}$$

$$\frac{d}{dt} P(t) = k_3 \cdot A \text{ substitute, } A = k_1 \cdot \frac{A^2}{k_2 \cdot A + k_3} \rightarrow \frac{d}{dt} P(t) = k_3 \cdot k_1 \cdot \frac{A^2}{k_2 \cdot A + k_3}$$

$$\frac{d}{dt} P(t) = k_3 \cdot k_1 \cdot \frac{A^2}{k_2 \cdot A + k_3} \text{ substitute, } k_2 \cdot A + k_3 = k_2 \cdot A \rightarrow \frac{d}{dt} P(t) = k_3 \cdot k_1 \cdot \frac{A}{k_2}$$

$$\frac{d}{dt} P(t) = k_3 \cdot k_1 \cdot \frac{A^2}{k_2 \cdot A + k_3} \text{ substitute, } k_2 \cdot A + k_3 = k_3 \rightarrow \frac{d}{dt} P(t) = k_1 \cdot A^2$$

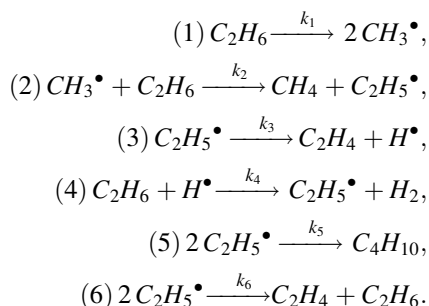
Fig. 2.18 The analysis of the monomolecular reaction mechanism

considerably facilitated under the conditions of small distances between molecules, which have no time to react.

It should be noted that, despite the made assumptions, the *Lindemann* theory qualitatively fits the experimental data predicting the change of the reaction order with the pressure change.

The steady-state concentration method is widely used for an analysis of kinetic mechanisms of complex reactions. In particular, this method plays an important role in the chain reaction theory.

For example, a large number of theoretical kinetic models have been suggested for describing ethane thermal cracking. Let us consider one of simplified mechanisms



As one can see, formation of end products – ethylene, butylene, and hydrogen – proceeds involving the intermediates – radicals $CH_3^\bullet$, $H^\bullet$, $C_2H_5^\bullet$. Let us solve the direct problem for this kinetic scheme in the steady-state approximation.

Firstly, it is necessary to derive the expressions for the intermediate steady-state concentrations. For this purpose, let us form the stoichiometric matrix and the rate vector and obtain the vector of right parts of the overall differential equation system for the given kinetic mechanism (Fig. 2.19).

The elements of the right part vector related to the rates of intermediate formation and consumption should be equated with zero and the obtained algebraic equations should be solved for the steady-state concentrations of the radicals. As a result, these operations (Fig. 2.19) yield

$$C_{CH_3^*} = 2 \frac{k_1}{k_2},$$

$$C_{C_2H_5^*} = \sqrt{\frac{k_1}{k_5 + k_6}} \sqrt{C_{C_2H_6}},$$

$$C_{H^*} = \frac{k_3}{k_4} \sqrt{\frac{k_1}{(k_5 + k_6) C_{C_2H_6}}}.$$

Next, the elements related to the stable reactants should be extracted from the vector of the right parts of the differential equations and the intermediate concentrations, which enter the equations, should be replaced with the obtained expressions. This stage of the symbolic evaluation is shown in Fig. 2.20. Thereby, by applying the steady-state concentration method, we obtained the reduced system of the differential equations describing the time-dependent concentration decrease or increase of the stable reactants.

Thereby, each of the equations entering the system has the form

$$\frac{d}{dt} C_{C_2H_6}(t) = -k_1 \frac{3k_5 + 2k_6}{k_5 + k_6} C_{C_2H_6}(t) - \frac{\sqrt{k_1} k_3}{\sqrt{k_5 + k_6}} \sqrt{C_{C_2H_6}(t)},$$

$$\frac{d}{dt} C_{CH_4}(t) = 2k_1 C_{C_2H_6}(t),$$

$$\frac{d}{dt} C_{C_2H_4}(t) = \frac{\sqrt{k_1} k_3}{\sqrt{k_5 + k_6}} \sqrt{C_{C_2H_6}(t)} + k_1 k_6 \frac{C_{C_2H_6}(t)}{k_5 + k_6},$$

$$\frac{d}{dt} C_{H_2}(t) = \sqrt{\frac{k_1}{k_5 + k_6}} k_3 \sqrt{C_{C_2H_6}(t)},$$

$$\frac{d}{dt} C_{C_4H_{10}}(t) = \frac{k_1 k_5}{k_5 + k_6} C_{C_2H_6}(t).$$

It is noticeable that only one function, $C_{C_2H_6}(t)$, enters the right part of the system, i.e. the current concentrations of methane, ethylene, hydrogen, and butylene are determined only by a value of the ethane current concentration.

The analytical solving the system at the initial condition $C_{C_2H_6}(0) = C_{C_2H_60}$ can be easily realized in Maple. Figure 2.21 demonstrates the worksheet part where the

ORIGIN := 1 $[C_2 \cdot H_6] = C_1$ $[CH_3^*] = C_2$ $[CH_4] = C_3$ $[C_2 \cdot H_5^*] = C_4$ $[H^*] = C_5$
 $[C_2 \cdot H_4] = C_6$ $[H_2] = C_7$ $[C_4 \cdot H_{10}] = C_8$

$$\alpha := \begin{pmatrix} -1 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & -1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 1 & 0 & 0 \\ -1 & 0 & 0 & 1 & -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & -2 & 0 & 1 & 0 & 0 \end{pmatrix} \quad r(k, C) := \begin{bmatrix} k_1 \cdot C_1 \\ k_2 \cdot C_1 \cdot C_2 \\ k_3 \cdot C_4 \\ k_4 \cdot C_1 \cdot C_5 \\ k_5 \cdot (C_4)^2 \\ k_6 \cdot (C_4)^2 \end{bmatrix} \quad rhs(k, C) := \alpha^T \cdot r(k, C)$$

$$rhs(k, C) \rightarrow \begin{bmatrix} (-k_1) \cdot C_1 - k_2 \cdot C_1 \cdot C_2 - k_4 \cdot C_1 \cdot C_5 + k_6 \cdot (C_4)^2 \\ 2 \cdot k_1 \cdot C_1 - k_2 \cdot C_1 \cdot C_2 \\ k_2 \cdot C_1 \cdot C_2 \\ k_2 \cdot C_1 \cdot C_2 - k_3 \cdot C_4 + k_4 \cdot C_1 \cdot C_5 - 2 \cdot k_5 \cdot (C_4)^2 - 2 \cdot k_6 \cdot (C_4)^2 \\ k_3 \cdot C_4 - k_4 \cdot C_1 \cdot C_5 \\ k_3 \cdot C_4 + k_6 \cdot (C_4)^2 \\ k_4 \cdot C_1 \cdot C_5 \\ k_5 \cdot (C_4)^2 \end{bmatrix}$$

$$rhs(k, C)_2 = 0 \text{ solve, } C_2 \rightarrow 2 \cdot \frac{k_1}{k_2} \quad rhs(k, C)_5 = 0 \text{ solve, } C_5 \rightarrow k_3 \cdot \frac{C_4}{k_4 \cdot C_1}$$

$$rhs(k, C)_4 = 0 \quad \begin{matrix} \text{substitute, } C_2 = 2 \cdot \frac{k_1}{k_2} \\ \text{substitute, } C_5 = k_3 \cdot \frac{C_4}{k_4 \cdot C_1} \\ \text{solve, } C_4 \end{matrix} \rightarrow \begin{bmatrix} \frac{1}{k_5 + k_6} \cdot [(k_5 + k_6) \cdot k_1 \cdot C_1]^{\frac{1}{2}} \\ \frac{-1}{k_5 + k_6} \cdot [(k_5 + k_6) \cdot k_1 \cdot C_1]^{\frac{1}{2}} \end{bmatrix}$$

$[CH_3^*] = 2 \cdot \frac{k_1}{k_2}$

$[C_2 \cdot H_5^*] = \sqrt{\frac{k_1}{k_5 + k_6}} \cdot (C_1)^{\frac{1}{2}}$

$[H^*] = \frac{k_3}{k_4} \cdot \sqrt{\frac{k_1}{k_5 + k_6}} \cdot (C_1)^{\frac{-1}{2}}$

Fig. 2.19 The symbolic evaluation of the intermediate steady-state concentrations

$\text{rhs_new}(k, C) := \text{stack}(\text{rhs}(k, C)_1, \text{rhs}(k, C)_3, \text{rhs}(k, C)_6, \text{rhs}(k, C)_7, \text{rhs}(k, C)_8)$

$$\begin{array}{l} \text{rhs_new}(k, C) \left\{ \begin{array}{l} \text{substitute, } C_2 = 2 \cdot \frac{k_1}{k_2} \\ \text{substitute, } C_4 = \sqrt{\frac{k_1}{k_5 + k_6}} \cdot (C_1)^{\frac{1}{2}} \\ \text{substitute, } C_5 = \frac{k_3}{k_4} \cdot \sqrt{\frac{k_1}{k_5 + k_6}} \cdot (C_1)^{-\frac{1}{2}} \\ \text{collect, } C_1 \end{array} \right. \rightarrow \left[\begin{array}{l} \left[(-3) \cdot k_1 + k_6 \cdot \frac{k_1}{k_5 + k_6} \right] \cdot C_1 - k_4 \cdot (C_1)^{\frac{1}{2}} \cdot \frac{k_3}{k_4} \cdot \left(\frac{k_1}{k_5 + k_6} \right)^{\frac{1}{2}} \\ 2 \cdot k_1 \cdot C_1 \\ k_3 \cdot \left(\frac{k_1}{k_5 + k_6} \right)^{\frac{1}{2}} \cdot (C_1)^{\frac{1}{2}} + k_6 \cdot \frac{k_1}{k_5 + k_6} \cdot C_1 \\ k_4 \cdot (C_1)^{\frac{1}{2}} \cdot \frac{k_3}{k_4} \cdot \left(\frac{k_1}{k_5 + k_6} \right)^{\frac{1}{2}} \\ k_5 \cdot \frac{k_1}{k_5 + k_6} \cdot C_1 \end{array} \right]$$

Fig. 2.20 Deriving the right part of the reduced differential equation system for ethane cracking

```
[> restart;
> R1:=dsolve({diff(C2H6(t), t)=-alpha*C2H6(t)-beta*C2H6(t)^(1/2),
C2H6(0)=C2H6[0]}):
> assign(R1);
> Ethane(t)=allvalues(C2H6(t));
```

$$\text{Ethane}(t) = \frac{\left(-\beta + e^{\left(-\frac{\alpha t}{2} \right)} \sqrt{C2H6_0} + e^{\left(-\frac{\alpha t}{2} \right)} \beta \right)^2}{\alpha^2}$$

Fig. 2.21 Derivation of the equation for the source reactant kinetic curve

curve equation for ethane is derived by means of `dsolve`. So as to avoid excessively awkward constructions, the following symbols are introduced

$$k_1 \frac{3k_5 + 2k_6}{k_5 + k_6} = \alpha,$$

$$\frac{\sqrt{k_1} \cdot k_3}{\sqrt{k_5 + k_6}} = \beta.$$

The expression for the current ethane concentration is next substituted into the rest of the equations of the reduced ODE system and their solution yields expressions for the last of the stable substances taking part in the overall process

$$C_{CH_4}(t) = 2k_1 \int_0^t C_{C_2H_6}(u) du,$$

$$C_{C_2H_4}(t) = \beta \int_0^t \left(\sqrt{C_{C_2H_6}(u)} + \frac{k_6}{k_3^2} C_{C_2H_6}(u) \right) du,$$

$$C_{H_2}(t) = \beta \int_0^t \sqrt{C_{C_2H_6}(u)} du,$$

$$C_{C_4H_{10}}(t) = \frac{\beta^2 k_5}{k_3^2} \int_0^t C_{C_2H_6}(u) du.$$

Here, u is a auxiliary value. Now, it is possible to evaluate the kinetic curves for all the reactants. Of course, information about the numerical values of the rate constants of all the steps are needed for this purpose. Such information can be found in reference literature but to use kinetic databases available in the global network is the simplest. A quite reliable source is the database of National Institute of Standards and Technology (<http://www.kinetics.nist.gov>). After a short search, the temperature dependencies of the constants $k_1 - k_4$ are found,

$$k_1 = 4.26 \times 10^{16} e^{-\frac{44579}{T}},$$

$$k_2 = 1.65 \times 10^9 \left(\frac{T}{298} \right)^{4.25} e^{-\frac{3890}{T}},$$

$$k_3 = 8.85 \times 10^{12} e^{-\frac{19469}{T}},$$

$$k_4 = 1.71 \times 10^{12} \left(\frac{T}{298} \right)^{2.32} e^{-\frac{3414}{T}}.$$

The rate constants for ethyl radical recombination in steps (5) and (6) do not depend on temperature,

$$k_5 = 1.15 \times 10^{13}; k_6 = 1.45 \times 10^{12}.$$

Finally, Fig. 2.22 illustrates the kinetic curve behaviour for the source reactant and the end product of ethane thermal decomposition. The calculations assume that the process proceeds at a temperature of 1,100 K and at an initial pressure of the gas mixture 2 atm. One should remember that, in this case, it is considered an approximate solution obtained in the framework of the approximation about a steady-state course of the process.

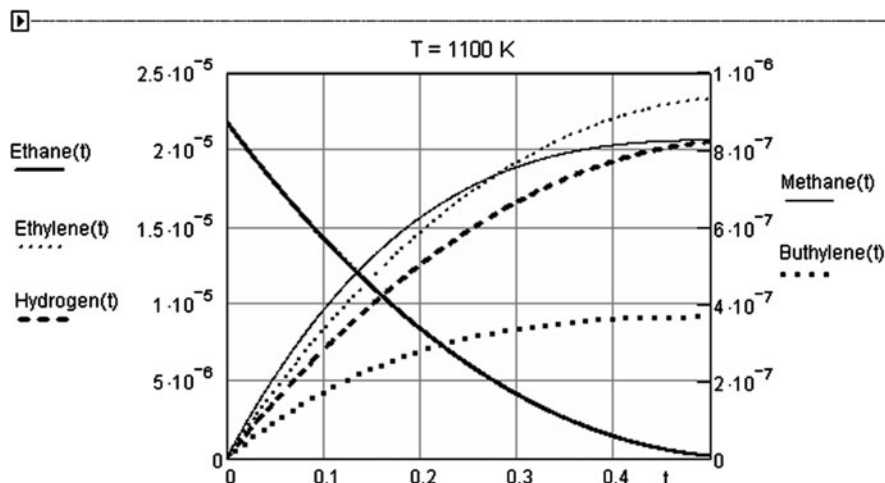


Fig. 2.22 The kinetic curves of the stable participants of the ethane cracking process

2.4.2 The Quasi-Equilibrium Approximation: Enzymatic Reaction Kinetics

Let us refer again to kinetic scheme (2.8) describing the consecutive reaction with the first step being reversible. If the equilibrium described by the constants k_1 and k_2 is established quickly, i.e. the step resulting in the end product is slow, the quasi-equilibrium principle is applicable in this case. According to this principle, the concentration of intermediate B practically does not differ from its equilibrium value owing to the hard-to-disturb equilibrium and can be expressed in terms of the ratio of the constants k_1 and k_2

$$K = k_1/k_2 = C_B/C_A.$$

Consequently,

$$C_B = \frac{k_1}{k_2} C_A,$$

and the rate of product C formation is given by

$$r_C = k_2 C_B = k_1 C_A.$$

Thus, the quasi-equilibrium principle should be obeyed provided the condition $k_3 \ll k_2$ is met. The corresponding calculation (Fig. 2.23) confirms this assumption.

The quasi-equilibrium principle gained a widespread practical use in *enzyme kinetics*, a branch of chemical kinetics describing catalytic reactions involving

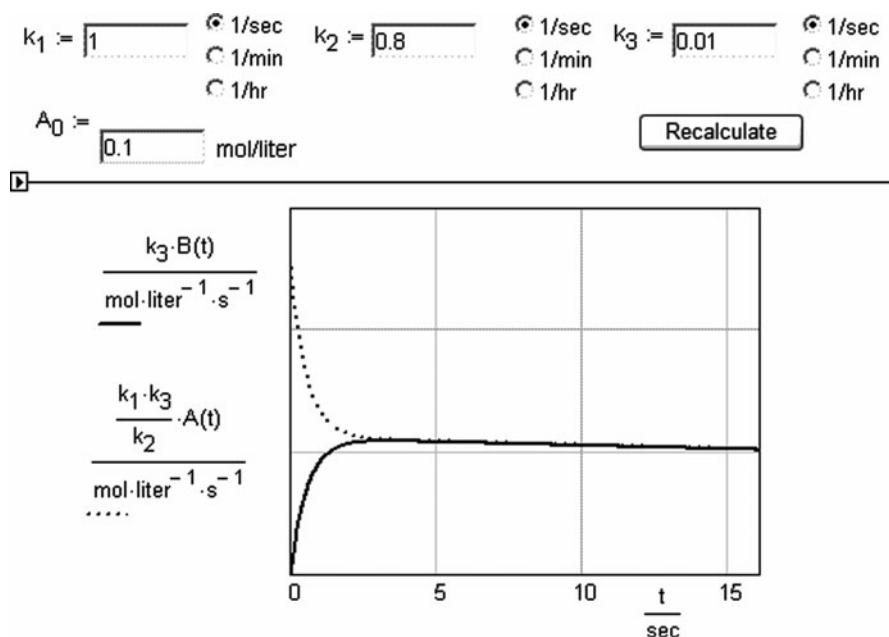
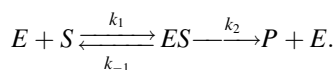


Fig. 2.23 Checking the quasi-equilibrium principle

enzymes. Enzymes are biological catalysts, protein molecules, as a rule. This is a particular type of reactions characterized by high enzyme effectiveness with respect to catalyzed processes and high selectivity of catalysts. Knowledge of enzyme reaction kinetics is necessary for understanding processes occurring into living organisms.

The scheme for the simplest enzyme reaction is



Here, E is an enzyme, S is a reactant (a substrate), P is a reaction product, ES is an enzyme–substrate complex. The process provides for reversible ES formation followed by its decay into the reaction product with simultaneous enzyme regeneration. Provided the step of product formation is slow ($k_2 \ll k_{-1}$), the reaction kinetics can be described in the framework of the quasi-equilibrium principle.

Thus, the quasi-equilibrium concentration C_{ES} of the enzyme–substrate complex is related to the rate constants k_1 and k_{-1} as well as to the concentrations of the enzyme C_E and the substrate C_S by

$$\frac{k_1}{k_{-1}} = \frac{C_E C_S}{C_{ES}}.$$

The concentration C_{ES} can be deduced from this relationship and substituted into the equation for the formation rate of end product P

$$r_P = k_2 C_{ES}.$$

The enzyme fraction bound in the complex cannot be found experimentally, therefore, the following calculations use the material balance equation

$$C_{ES} + C_E = C_{E_0},$$

where C_{E_0} is an overall enzyme concentration. With the help of the last three relationships, one can obtain the known *Michaelis–Menten* equation

$$r_P = \frac{k_2 C_{E_0} C_S}{K_M + C_S}. \quad (2.10)$$

Derivation of the *Michaelis–Menten* equation using the suits of the Mathcad symbolic redactor is given in Fig. 2.24. Here, K_M is the *Michaelis constant* whose physical meaning corresponds to the dissociation constant for the enzyme–substrate complex, $K_M = k_{-1}/k_1$.

Interpretation of (2.10) leads to quite interesting conclusions. Thus, if the substrate concentration is low ($K_M \gg C_S$), the equation reduces to the form

$$r_P \approx \frac{k_2 C_{E_0} C_S}{K_M}$$

On the contrary, at high substrate concentrations $K_M \ll C_S$ and

$$r_P \approx k_2 C_{E_0}.$$

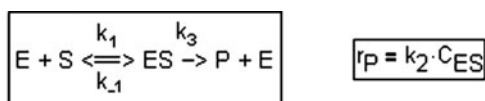
Thereby, at low S concentrations the reaction has an order of 1 with respect to the substrate. When transferring to high concentrations, the reaction rate stops depending on a concentration, i.e. the reaction changes its order into zero. The high substrate concentrations favor the maximum reaction rate

$$r_{\max} = k_2 C_{E_0}. \quad (2.11)$$

Figure 2.24 illustrates the general behaviour of the reaction rate vs. the current substrate concentration.

Taking into account expression (2.11), (2.10) can be rewritten in the following forms

$$\frac{1}{r_P} = \frac{1}{r_{\max}} + \frac{K_M}{r_{\max}} \cdot \frac{1}{C_S}, \quad (2.12)$$



$$\frac{k_1}{k_{-1}} = \frac{C_{ES}}{C_E \cdot C_S} \text{ substitute, } C_E = C_{E0} - C_{ES} \rightarrow \frac{k_1}{k_{-1}} = \frac{C_{ES}}{C_S \cdot (C_{E0} - C_{ES})}$$

$$\frac{k_1}{k_{-1}} = \frac{C_{ES}}{C_S \cdot (C_{E0} - C_{ES})} \text{ solve, } C_{ES} \rightarrow \frac{C_S \cdot C_{E0} \cdot k_1}{k_{-1} + C_S \cdot k_1}$$

$$r_P = k_2 \cdot C_{ES} \text{ substitute, } C_{ES} = \frac{C_S \cdot C_{E0} \cdot k_1}{k_{-1} + C_S \cdot k_1} \rightarrow r_P = \frac{C_S \cdot C_{E0} \cdot k_1 \cdot k_2}{k_{-1} + C_S \cdot k_1}$$

$$r_P = \frac{C_S \cdot C_{E0} \cdot k_2}{\frac{k_{-1}}{k_1} + C_S} \text{ substitute, } \frac{k_{-1}}{k_1} = K_M \rightarrow r_P = \frac{C_S \cdot C_{E0} \cdot k_2}{C_S + K_M}$$

$$C_{E0} := 1.214 \times 10^{-7} \quad k_2 := 10 \quad K_M := 4.815 \cdot 10^{-4} \quad C_S := 10^{-5}, 0.0001 \dots 0.015$$

$$r_P(C_S) := \frac{C_S \cdot C_{E0} \cdot k_2}{C_S + K_M}$$

$$r_{\max} := k_2 \cdot C_{E0}$$

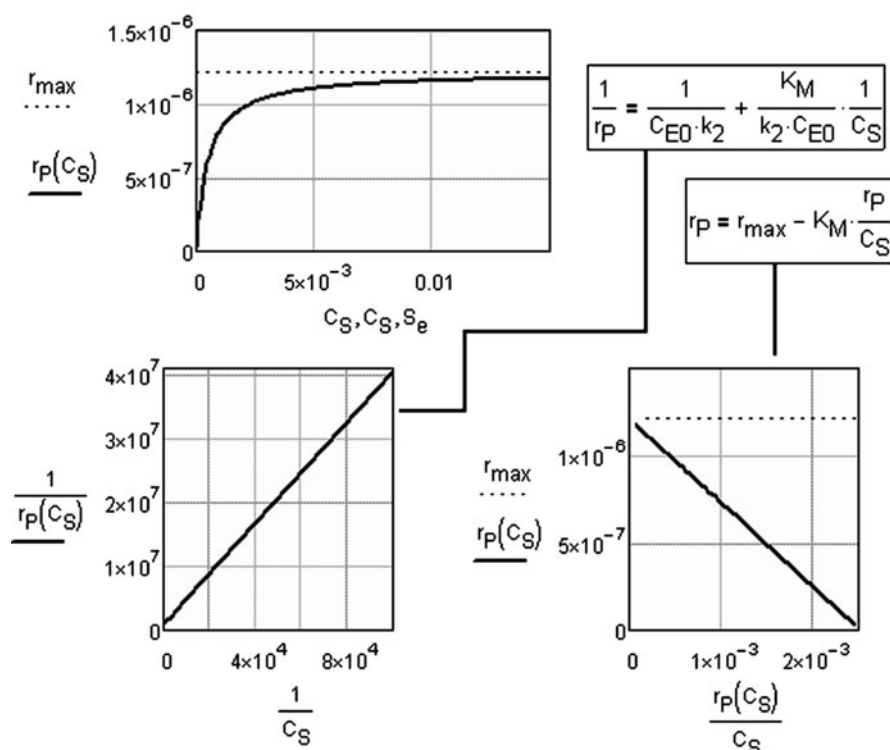


Fig. 2.24 Derivation of the kinetic equations for the enzyme reaction

$$r_P = r_{\max} - K_M \frac{r_P}{C_S}. \quad (2.13)$$

Consequently, the curve of a rate vs. a concentration is linearized on $r_P^{-1} - C_S^{-1}$ coordinates (*Lineweaver–Burk* coordinates) or on $r_P - r_P/C_S$ coordinates. The both types of coordinates can be used when treating experimental data for solving the inverse kinetic problem. The method of initial rates, when initial reaction rates are measured at different initial substrate concentrations, is used for this purpose.

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