

Chapter 3. “Numerical solution of the direct problem in chemical kinetics”

from the book V.Korobov, V.Ochkov “Chemical Kinetics: Introduction with Mathcad/Maple/MCS” - Moscow, 2009

Previously discussed analytical methods for solving the direct problem in chemical kinetics are not sufficient for analysis of different reaction kinetic schemes. First, even given the mathematical model represented by an ODE system, it is not always possible to integrate the equations analytically. The reason for that may be just an absence of such a solution. This refers primarily to a large number of kinetic models in which differential equations are non-linear relative to the sought functions.

Second, if the analytical solution is obtained, it is often too lengthy and awkward.

Finally, there is a large class of real mathematical models that are described by partial differential equation sets¹, which cannot be integrated numerically. Thus, the series of mathematical problems that can be solved with the previously discussed numerical integration methods is quite narrow. That is why, in order to solve the direct problem, we have to rely on more universal approaches. Such approaches are based on using numerical integration of differential equations and systems.

3.1. Given/Odesolve solver in Mathcad system

Among the built-in tools of the Mathcad suite an important role belongs to those designed for the numerical solving ordinary differential equations (ODEs) and their systems. Let's look through these tools starting with the solving unit GIVEN/ODESOLVE. The ODESOLVE function first appeared in Mathcad 2000 Pro. On default this function used Runge-Kutta method of the fourth-level of precision².

The organization of the GIVEN/ODESOLVE solver resembles greatly that of the GIVEN/FIND solving block: it starts with the GIVEN keyword. An ODE or a system as well as the initial conditions should be placed in the solver body. The solving is performed with a call up of built-in function ODESOLVE using the following format:

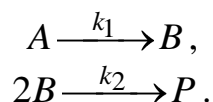
```
ODESOLVE(x, b, [steps]),
```

where x is the unknown, and b is the upper integration limit. The last parameter, $steps$, determines the number of integration steps and is optional. If this parameter is absent, the number of steps is set up automatically.

As an example, let's calculate a kinetic curve for an intermediate in a consecutive reaction where the second step is of the second order:

¹ We do not discuss such mathematical models in this book.

² In this book we will not discuss the essence of such and such numerical integration methods. This information is available in virtually all handbooks on numerical methods.



Analytical solution of this problem was discussed in the *chapter 1.3.2*, so we can compare numerically- and analytically-obtained results.

The way of using GIVEN/ODESOLVE solver and the results of its work are shown in fig. 3.1. The following values were used: initial concentration $A = 0.5M$, rate constants $k_1 = 0.05 s^{-1}$ and $k_2 = 0.1 M^{-1} \cdot s^{-1}$. Referring to fig. 3.1, the kinetic curve calculated numerically (dots) matches the curve calculated using analytical formula (line). The authors want to point out that during the assigning of the results of symbolic computation one should use only the name of the desired function (without argument). For the construction of a graph both function name and its argument are specified fig. 3.1).

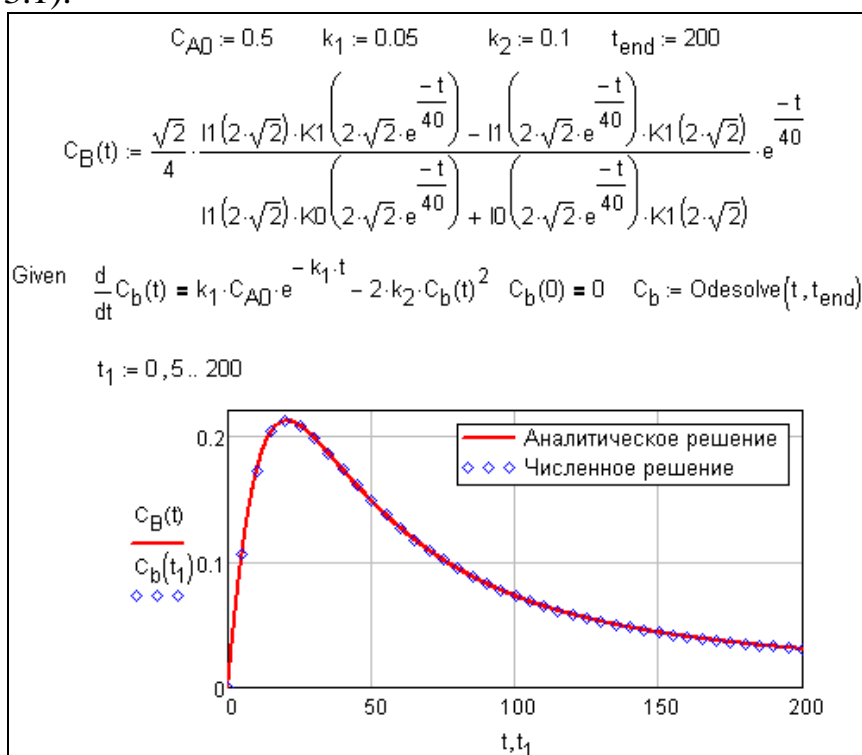
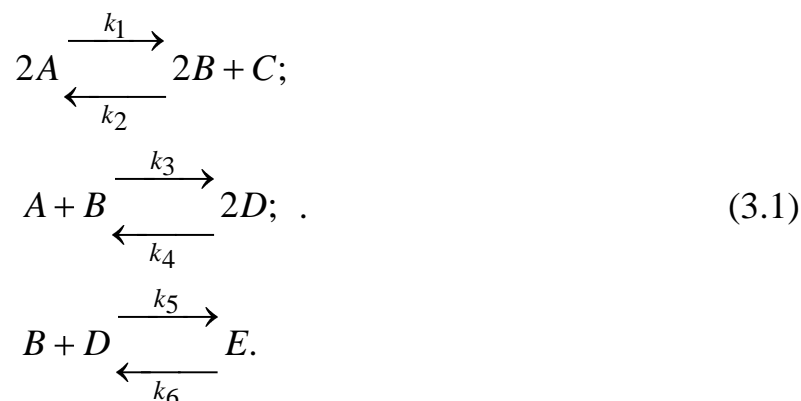


Fig. 3.1. Kinetic curve calculation for an intermediate in a consecutive second-order reaction using ODESOLVE function

The results of this example allow one to think that the ODESOLVE function is a sufficient tool for solving the direct kinetic problem. Now we proceed to a numerical solution of an *ordinary differential equation* (ODE) set using a solver. Solving process for an ODE set does not differ much from that for a single ODE: all equations in the set as well as the starting condition equalities are given in the solver. The only difference is in the number of arguments that ODESOLVE function should have. An array of desired function names is required for solving sets of equations. The variable, where the calculation result is stored, is an array of function names as well. Below is an example of a numerical calculation of all component concentrations in a hypothetical multi-step reaction.



We can see that the process goes through 6 elementary steps with 5 compounds; and most of the reactions have order higher than first. Finding the analytical solution of the direct problem is barely possible in this case. However, having numerical integration tools we do not need an analytical approach.

The solution of this example is shown in fig. 3.2. One can see that the use of ODESOLVE function is rather simple.

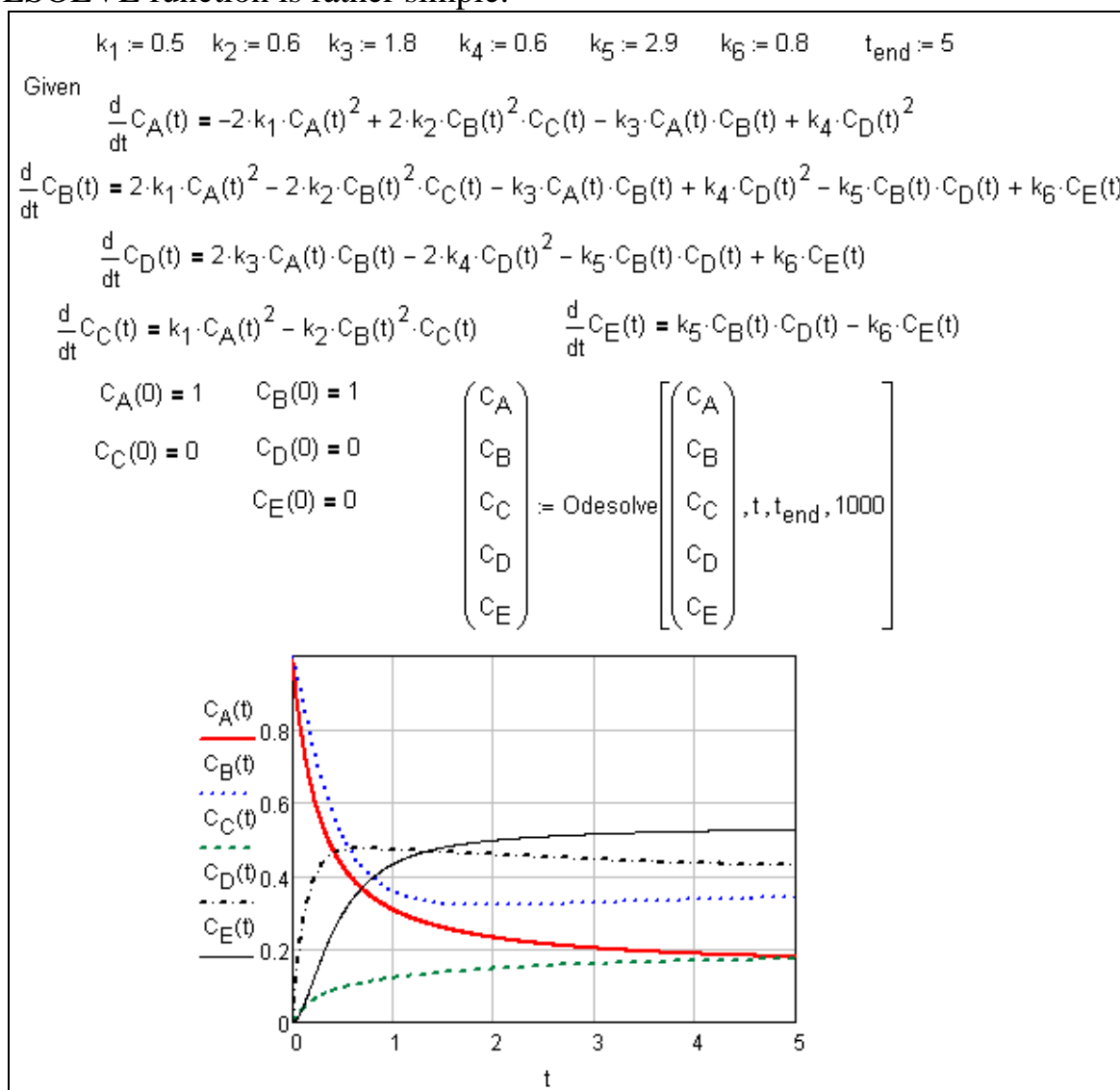


Fig. 3.2. Calculation of the kinetic curves for all components in a multi-step reaction using ODESOLVE function

Working with ODESOLVE the user can choose an algorithm for the numerical ODE solution. If the cursor is above ODESOLVE keyword, the right-click will activate the corresponding context menu (fig. 3.3). In Mathcad 2001–13 the user could choose between integration with a fixed (Fixed) or adaptive (Adaptive) step as well as a special method for stiff systems integration (Stiff). A new option, Adams/BDF, was added in Mathcad 14.

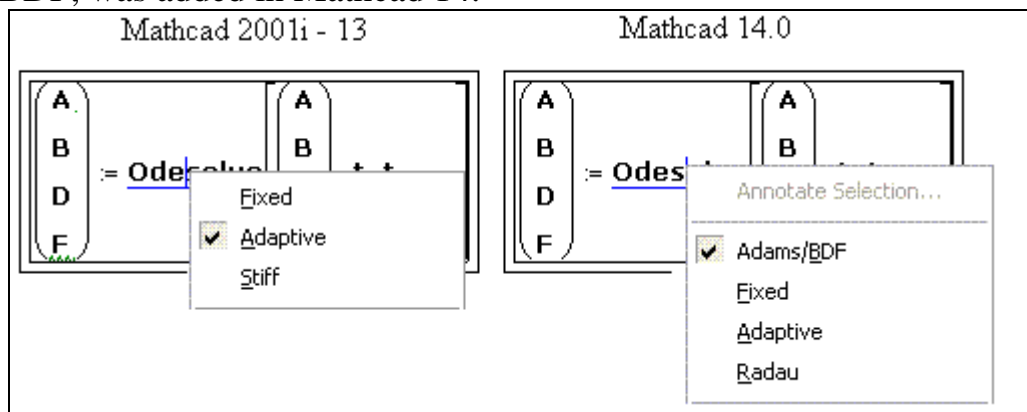
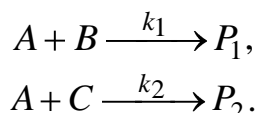


Fig. 3.3. Choosing an ODESOLVE algorithm in different Mathcad versions.

An obvious advantage of the GIVEN/ODESOLVE solver is that differential equations and ODE sets are written in the usual manner. That is why Mathcad documents designed for kinetic problems are rather clear. Another feature of the ODESOLVE solver is the possibility to use not only differential equations but also usual algebraic ones.

For example, let's consider solving the direct problem for a parallel reaction with the following mechanism:



Here reagent A is consumed in two parallel steps through interaction with reagents B and C. Each step has the second order. To find kinetic curves for all the compounds in this reaction it is enough to use a mathematical model consisting of two differential and three algebraic equations (the latter represent the material balance of the reaction system):

$$\frac{dC_B}{dt} = -k_1 C_A C_B,$$

$$\frac{dC_C}{dt} = -k_2 C_A C_C,$$

$$C_{A_0} - C_A = C_{B_0} - C_B + C_{C_0} - C_C,$$

$$C_{P_1} = C_{B_0} - C_B,$$

$$C_{P_2} = C_{C_0} - C_C(t).$$

All equations can be put in the solver without changes. The corresponding numerical solution is shown in fig. 3.4.

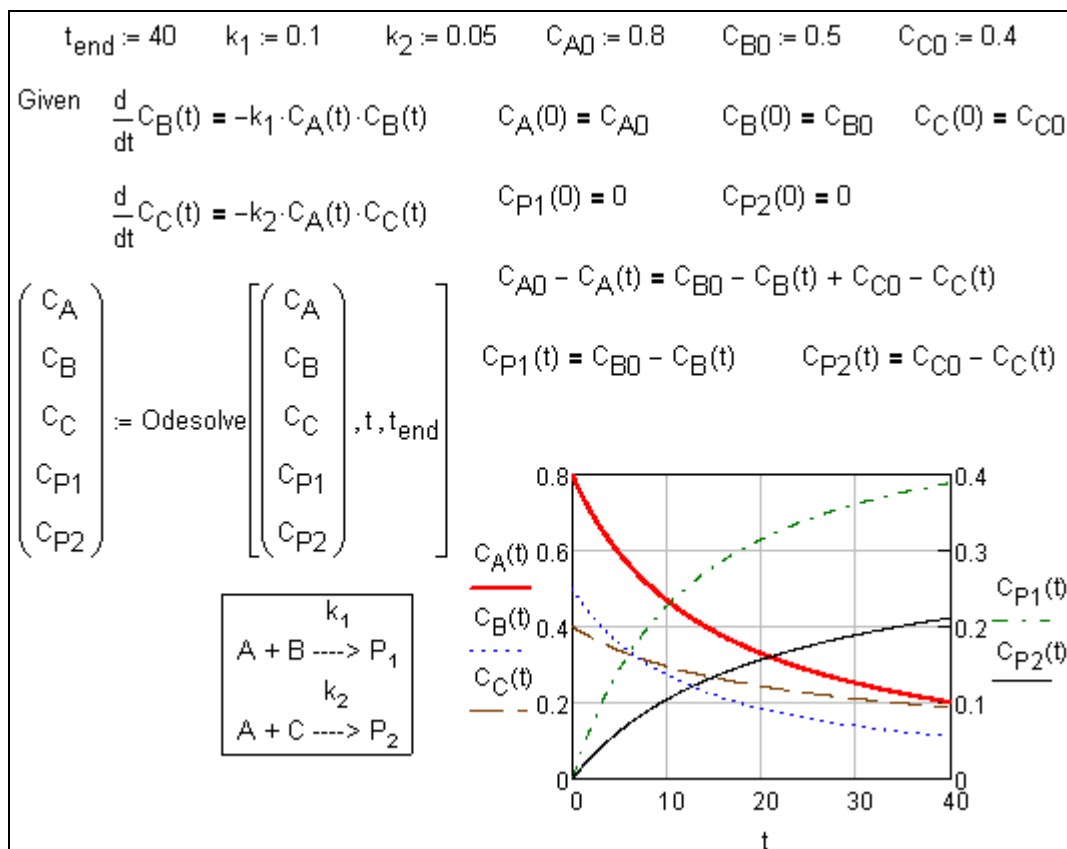


Fig. 3.4. Solving a system of “differential—algebraic” equations

So far, we have considered the problem of calculating kinetic curves for compounds. In mathematics this is called a **Cauchy problem**. It is known that for the Cauchy problem entry conditions are given, i.e. the value(s) of the desired function $y(x)$ at point $x=x_0$. In kinetics, as a rule, this point corresponds to the starting point of a reaction. Often one needs to find a partial solution of a differential equation using known function values in several points. Such kind of problems is called a **boundary-value problem (boundary problem)**.

The *two-point boundary problem* may be exemplified by the calculation of the kinetic curve for an intermediate in a consecutive reaction $A \rightarrow B \rightarrow P$ using known values of concentration at two moments of time (fig. 3.5). Assume the initial A concentration $C_{A0} = 1 \text{ M}$, rate constants $k_1 = 0.008 \text{ s}^{-1}$, $k_2 = 0.004 \text{ s}^{-1}$, and the concentration of an intermediate B after 7.2 and 445.1 s from the beginning of the reaction $C_b = 0.05 \text{ M}$. To calculate the kinetic curve for the compound B we will use the equation:

$$dC_B \text{ (over } dt) = k_1 C_{A0} e^{-k_1 t} - k_2 C_B \text{ (over } dt),$$

that is converted into:

$$d^2 C_B \text{ (over } dt) = -k_1^2 C_{A0}^2 e^{-k_1 t} - k_2 dC_B \text{ (over } dt).$$

The solution of this boundary problem is given in fig. 3.5 and it does not require additional explanation.

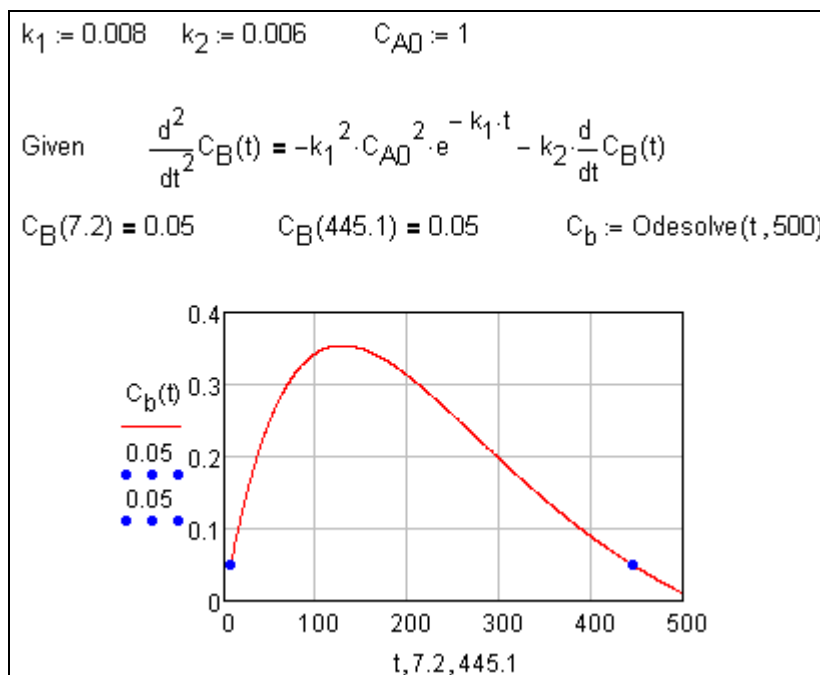


Fig. 3.5. Solving a boundary-value problem with solver

3.2. Built-in Mathcad integrators

In addition to Given/Odesolve solver, one can use built-in Mathcad suite integrators for solving the direct kinetic problem. These integrators are designed specifically for the numerical solving of ODEs and ODEs sets. There are several built-in functions of this kind. It is important to mention that each of the integrators requires right-hand member array of the ODEs set. Recall that the mathematical model for a complex reaction is obtained through multiplying the stoichiometric array by the rate array. The result of this operation is the array of the ODE set right-hand values. That is why built-in integrators are very convenient for solving kinetic problems with stoichiometric arrays of high dimensionality.

We will begin the learning of the integrators with the `rkfixed` function. It implements the fourth-order Runge-Kutta method (rk) with fixed step of integration (fixed). According to Mathcad syntax this function has five required arguments:

$$\text{rkfixed}(v, x1, x2, \text{npoints}, f),$$

where v is the initial values vector; $x1$ and $x2$ — independent variable values that determine the interval of integration; npoints — the integration steps quantity; f — the array function of the ODE set right-hand values.

Creation of the array function f requires following a specific procedure. Usually this function is declared right before `rkfixed` using the following syntax:

$$f(t, x) := [\text{array of the ODE set right-hand values}],$$

where t is the independent variable and x is the desired functions array. The right-hand part of this construction is an array of the ODE set right-hand values; and each of these functions is represented by an index variable x , i.e. x_0, x_1 etc.

The quantity of the array x elements as well as the quantity of the right-hand values is equal to the quantity of equations in the system. Let's clarify how `rkfixed` works by an example of a numerical solution of the direct problem for a three-step consecutive chemical reaction (fig. 3.6).

In the beginning, the right-hand value array `Model(k,x)` is defined. Current concentrations of the compounds A, B, C, D are given as x_1, x_2, x_3, x_4 (here 1, 2, 3, 4 are vector indices, not lettered ones!) After assigning the rate constant values, a function `F(t,x)` is declared. The first argument must be an independent variable — time. This declaration allows the `rkfixed` integrator to understand the function `F(t,x)`. The numerical calculation result is stored in a matrix `S`. Based on the rows and columns quantities in this matrix one may conclude: the solution matrix has $(n+1)$ columns if the set has n equations. It is easy to see that the first column starts with a value $t_n=0$ and ends with a value $t_k=100$. The matrix has $(N+1)$ rows for N integration steps. The second column contains the value of the variable x_2 at each integration step. In this case these are the values of the reagent A concentration. Correspondingly, the 3rd, 4th and 5th columns represent concentrations of the reagents B, C and D . Thus, the matrix `S` give a pictorial view of the reaction mixture changes over time. Finally, we can make a graphical representation of the calculation results as kinetic curves for each reagent.

Thereby, Mathcad tools for numerical solution of differential equation sets allow one to calculate quickly kinetic curves of all reactants in a complex chemical process. As the independent variable in chemical problems is time t , discussed methods can be used in modeling any time function (having postulated a differential model for the process). One can find many analogies of the kinetic models of chemical reactions in other fields of knowledge (microbiology, sociology etc.) It is useful to discuss the corresponding examples in order to form some practical skills in creating differential models.

Let's consider one of such problems. Certain microorganisms propagate in proportion to the colony size (with an aspect ratio k) but at the same time produce some excrement, which is a poison for them.

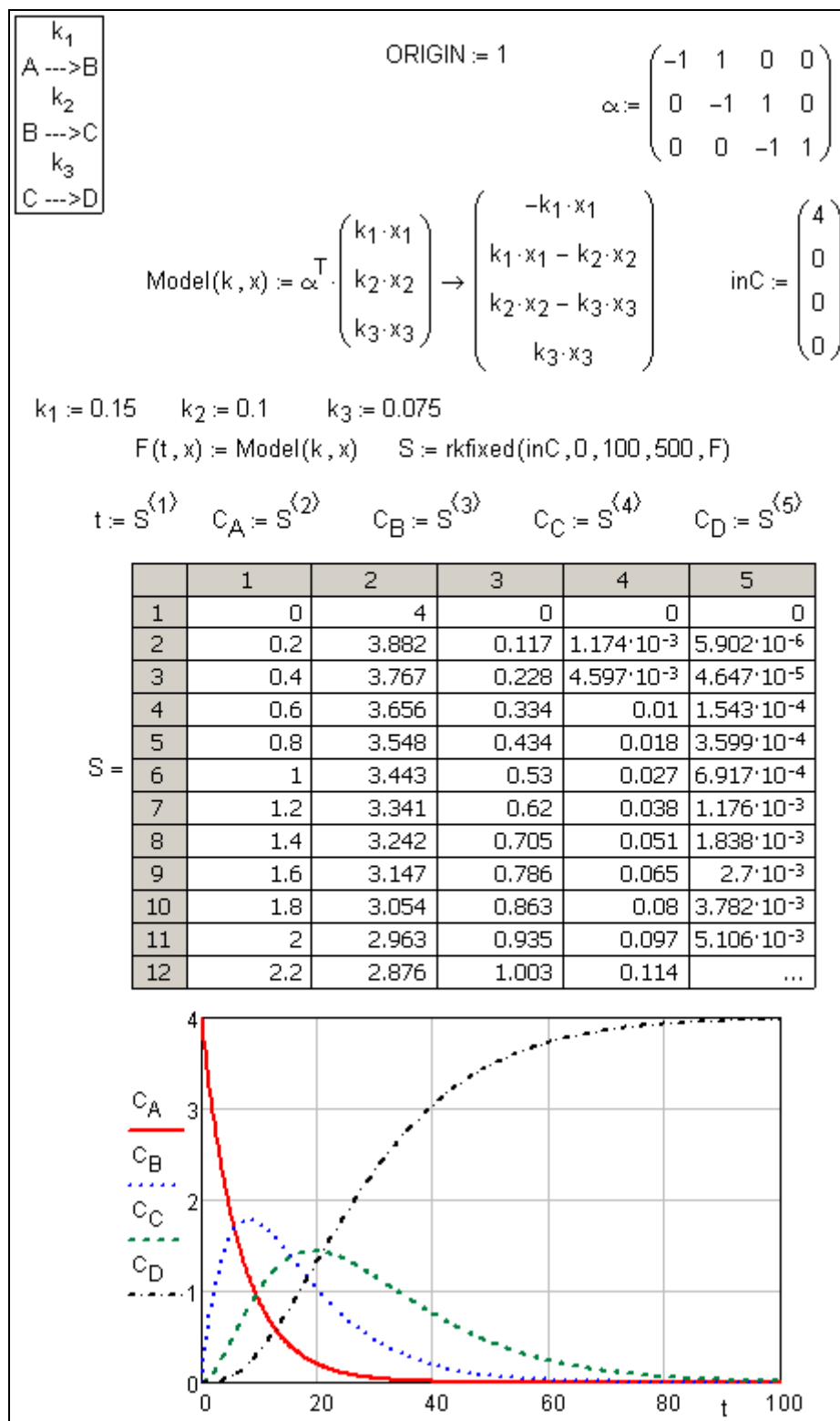


Fig 3.6. Numerical solution of the direct problem for a consecutive reaction with two intermediates

The rate of the colony disappearance is proportional to the amount of poison and current microorganism population with an aspect ratio k_1 . The poison formation rate is proportional to the number of microorganisms (with a ratio k_2). Suppose the initial colony size equals N_0 , and the amount of poison Z is 0 at the beginning. One is required to make the corresponding set of differential equations and solve it

numerically, and present graphically the microorganisms population trends along with the amount of poison in the system. Assume $k=0,1$; $k_1=0,0001$; $k_2=0,01$, $N_0=2000$.

First, we should create a differential equation set in accordance with the problem specifications. Changes in the microorganisms population is determined by an increase kN as a result of reproduction and a decrease $-k_1NZ$ due to poisoning. Therefore, the first differential equation of the system will be of this form:

$$dN / dt = kN - k_1NZ .$$

The rate of poison amount change will be described as

$$dZ / dt = k_2N .$$

A differential model for the process has been defined; now we can create a corresponding Mathcad document to solve the problem (fig. 3.7).

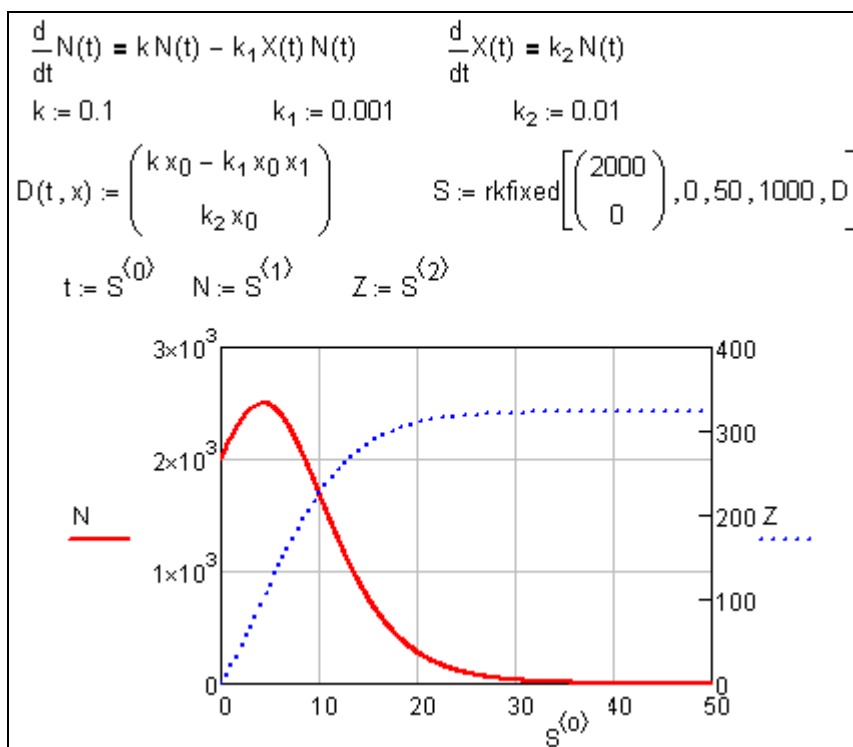


Fig 3.7. Microorganism population and poison amount trends

As the figure 3.7. implies, the number of microorganisms first increases with time, achieves the highest value at some point, and after that the colony becomes extinct. The curve $Z(t)$ is a typical saturation one. At the beginning, the poison accumulation rate is small, but it increases with the lapse of time until it reaches the maximum. Certainly, after full disappearance of the microorganisms the amount of poison stabilizes and becomes constant. A chemical analog for this model would be a complex chemical reaction where compounds N and Z participate in an intermediate

step. In this case, the compound Z is an autocatalyst for the decomposition of N in accordance with discussed mathematical correlations.

Further in the book we will see that a minor (at first sight) modification of the starting differential equations set and initial conditions may cause a significant change in the dynamic outlook of the solution.

One may often have a case when in order to obtain enough accurate result it is necessary to use a variable integration step: decreasing in the area of large derivative changes and, *vice versa*, increasing when the derivative changes slowly. This approach is implemented in an algorithm that function `Rkadapt` uses. During the work of this function the step of integration is adapted in accordance with the derivative trend in the selected interval of integration. Let's consider the following ODE system as an example:

$$\begin{aligned} \frac{dX}{dt} &= a - (b+1)X + X^2 Y \\ \frac{dY}{dt} &= bX - X^2 Y \end{aligned}$$

Further, we will discuss minutely this system which is a mathematical model of the widely-known kinetic scheme **bruesselator**. Now we will compare the results of its numerical solution using the functions `rkfixed` and `Rkadapt`.

The corresponding plots are shown in fig. 3.8. They show that using a fixed step can lead to an instable solution which can be interpreted wrongly from a physical point of view (dashed line). The function `Rkadapt`, as we can see, allows us to eliminate the mistakes of `rkfixed`, and reveals the true behavior of the desired function in the given independent variable range (due to an adaptable step of integration). In practice, `Rkadapt` is preferable in the solving of many direct problems, especially in cases when the starting kinetic model is non-linear.

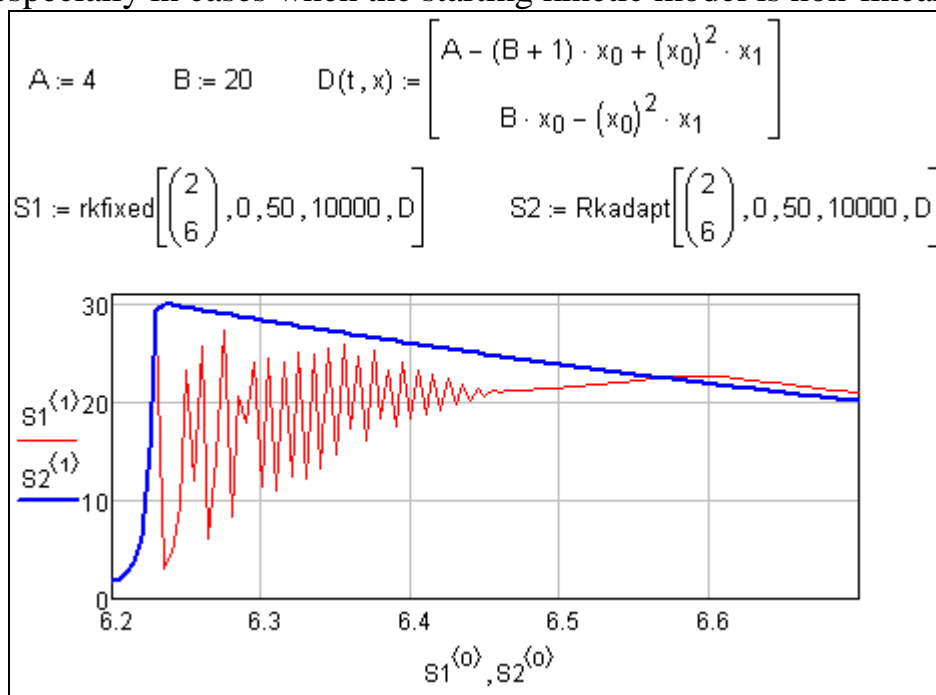
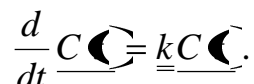


Fig 3.8. Comparison of the results for calculations with fixed step of integration (solid line) to an adaptive one (dashed line)

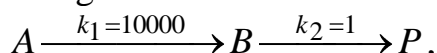
We also want to mention that the function `Rkadapt` requires the same five arguments specified in an `rkfixed` body. Even though integration utilizes a changeable step, the result will still be represented for evenly distributed points as specified by user.

There is one more circumstance related to a variety of built-in integrators. It is the existence of so-called *stiff* ODE sets. The concept of stiffness may be illustrated by the example of the kinetic equation for a multi-step reaction



It is considered that the mathematical model is stiff if among the eigenvalues λ_i of the rate constant matrix \underline{k} there exist such eigenvalues for which $\text{Re}(\lambda_i) \ll 0$. Usually this condition holds if the rate constants matrix has elements very different in modulo (three and more orders).

Let's consider the following kinetic scheme:



that can be described with only two differential equations in accordance with the stoichiometric matrix rank. The corresponding ODE set can be written as

$$\frac{d}{dt} \begin{pmatrix} C_A \begin{matrix} \curvearrowright \\ \curvearrowright \\ \curvearrowright \\ \curvearrowright \end{matrix} \\ C_B \begin{matrix} \curvearrowright \\ \curvearrowright \\ \curvearrowright \\ \curvearrowright \end{matrix} \end{pmatrix} = \begin{pmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{pmatrix} \begin{pmatrix} C_A \begin{matrix} \curvearrowright \\ \curvearrowright \\ \curvearrowright \\ \curvearrowright \end{matrix} \\ C_B \begin{matrix} \curvearrowright \\ \curvearrowright \\ \curvearrowright \\ \curvearrowright \end{matrix} \end{pmatrix}.$$

The eigenvalues vector for this matrix is equal to

$$\underline{\lambda} = \begin{pmatrix} -1000 \\ 1 \end{pmatrix},$$

which allows one to consider the mathematical model as a stiff one. In this case the integration should be performed using special built-in functions for stiff systems. Mathcad suite has integrators `Stiffb`, `Stiffc`, `Radau`, and starting from Mathcad 14 — an integrator `AdamsBDF`. Fig. 3.9 shows the Mathcad document illustrating the solution of the direct kinetic problem for a stiff model using several integrators.

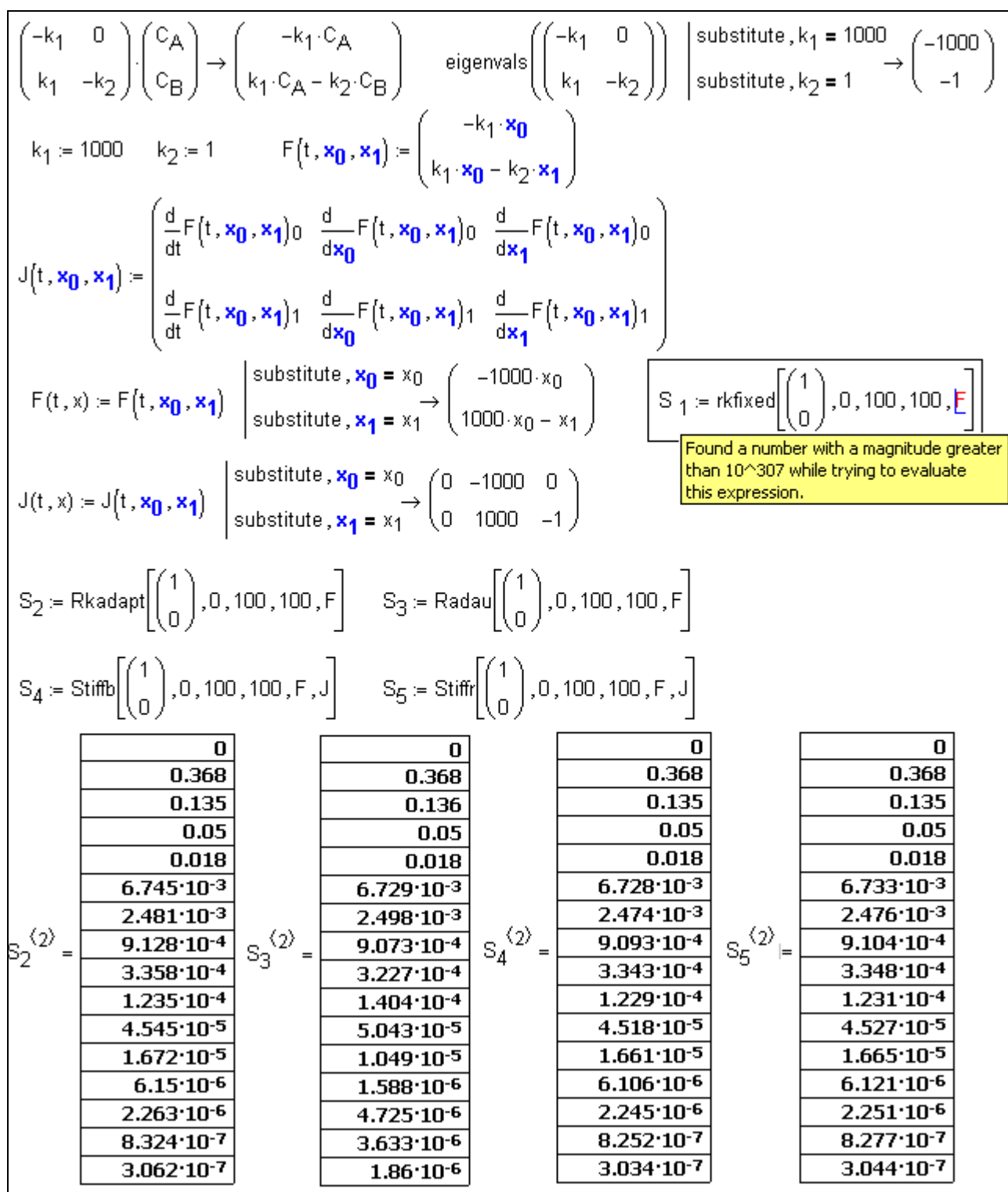


Fig 3.9. An example of a kinetic scheme described with a stiff set of differential equations (Mathcad 11.2)

As fig. 3.9 shows, the integrator rkfixed can not solve the problem at all. It shows a diagnostic message «Found a number with a magnitude greater than 10³⁰⁷ while trying to evaluate this expression». In this case the integrators Rkadapt, Radau, Stiffb, and Stiff are working but give different computation results for the chosen step of integration. One can find that a five-fold increase in the number of

steps virtually levels the results. However, the integration of more complex stiff sets still should be done by using the specially designed built-in functions

The functions `Stiffb` and `Stiffc` require an additional argument $J(t, x)$, which is a matrix of partial time (t , zero column) and the x vector derivatives for a kinetic function. A way to form the vector $J(t, x)$ is shown in fig. 3.9. It is worth mentioning that, in the early versions, this stage was done manually (paying attention to the fact that the symbol editor cannot differentiate expressions with index variables). The user had to transform the index variables into lettered ones and *vice versa* (see the fig. 3.9 where the index and lettered variables are formatted with different styles). Because of that the Mathcad 2001i version included the `Radau` function that did not require the argument $J(t, x)$. Although it was very convenient, the user had to accept some loss of precision. In the Mathcad 14 version the functionality of the `Radau` was expanded. In addition, this version had tools for automatization of the matrix $J(t, x)$ symbolic calculation.

3.3. The Maple system commands `dsolve`, `odeplot` in numerical calculations

The command `dsolve` of the Maple system was previously discussed as a method of analytical solution of the direct problem in chemical kinetics. This command also can be used for a numerical solving of ODEs or their sets. In this case one should use the following syntax:

```
dsolve({ode,ic}, numeric, vars, options)
```

Here `ode` is the differential equation (or ODE set) with the initial conditions `ic`. The option `numeric` is a directive for numerical computations (one may use the construction 'type=numeric' instead of the keyword `numeric`); `vars` is the desired function (or the desired function set in case of ODE set); `options` are additional options given in the keyword=value form.

The option `numeric` (or `type=numeric`) indicates that `dsolve` will return a numerical calculation result. The most important additional option is the `method`. It determines which numerical method will be used in the desired function search. The Maple system gives a choice among a variety of methods (see the list in table. 3.1).

On default, during a solution of the Cauchy problem the `dsolve` function automatically utilizes the Runge-Kutta method of the 4–5th order of accuracy. The major options are given in the table 3.2.

Table 3.1 – Numerical methods for solving ordinary differential equations in Maple[®] suite.

No.	The 'method' value	Numeric method used by
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\dsolve' solver

1. rk45	Runge-Kutta-Fehlberg method of the 4-5 th order of accuracy
2. classical or classical[foreuler]	Euler method
3. classical[heunform]	Modified Euler method using Heun's formula
4. classical[impoly]	Euler method subkind
5. classical[rk2]	Runge-Kutta method of the 2 nd order of accuracy
6. classical[rk3]	Runge-Kutta method of the 3 rd order of accuracy
7. classical[rk4]	Runge-Kutta method of the 4 th order of accuracy
8. classical[adambash]	Adams-Bashforth method
9. classical[abmoulton]	Adams-Bashforth-Moulton method
10. rosenbrock	Rosenbrock method
11. bvp	Numerical method to solve the b oundary v alue p roblem
12. dverk78	Runge-Kutta method of the 7-8 th order of accuracy
13. lsode or lsode[choice], where choice can be adamsfunc, adamsfull, adamsdiag, adamsband, backfunc, backfull, backdiag, backband	Modification of the Adams method for the solving of stiff ODE and their sets
14. gear, gear[bstoer], gear[polyextr]	Gear method and its modifications
15. taylorseries	Method utilizing the Taylor series expansion of integrand

Table 3.2 – Some major options for the dsolve command used in numerical calculations

Option	Purpose
'output' =	Controls the output order of

keyword or array	the calculation results. Can have the symbol values 'procedurelist', 'listprocedure', as well as 'array' or 'Array'. By default 'output'= procedurelist.
'stop_cond' = list	Controls the process of computation finishing when the 'list' conditions are met.
'range' = numeric..numeric	Determines the independent variable range (the length of the integration interval).
'stiff'=boolean	This option is given as a Boolean expression. For example, if 'stiff'=true, the equation is considered stiff and the default 'method' value is set to 'rosenbrock' instead of 'rk45'.

An important component of using the dsolve function in numerical calculations is the output order of the results. In particular, when the following construction is being used:

```
>dsol:=dsolve({sys1,invalues},numeric);
```

only a message about the successful procedure implementation is displayed:

```
dsol:=proc(rkf45_x)...end proc
```

After that, the user has to decide how the results should be visualized. It is possible to print the answer in the form of individual values of the desired function, an array, etc. However, the most visual output form is the graphical one. The plotting of the results is provided by the command odeplot from the graphical library plots. Figs. 3.10 and 3.11 show a solution of the differential equation set, which describes the kinetics of the first-order reversible reaction $A \rightleftharpoons B$ with arbitrary rate constant values.

```

10 Fig_3_10_and_3_11_DirectProblem_Maple10.mws - [Server 1]
[> restart ;
> sys1:=diff(A(t),t)=-k[1]*A(t)+k[2]*B(t),diff(B(t),t)=-k[2]*B
(t)+k[1]*A(t);
      sys1 :=  $\frac{d}{dt} A(t) = -k_1 A(t) + k_2 B(t), \frac{d}{dt} B(t) = -k_2 B(t) + k_1 A(t)$ 
[> invalues:=A(0)=1,B(0)=0.1: k[1]:=0.05: k[2]:=0.025:
> dsol1:=dsolve({sys1,invalues},numeric,range=0..4);
      dsol1 := proc(x_rkf45) ... end proc
Значения искомых функций (концентраций A и B при выбранных значениях независимой
переменной t)
> dsol1(0.005);
      [t = 0.005, A(t) = 0.999762544525681028, B(t) = 0.100237455474319170]
> dsol1(0.05);
>
      [t = 0.05, A(t) = 0.997629447563644246, B(t) = 0.102370552436355650]
Вывод результатов в виде массива (output=array)
> dsol2:=dsolve({sys1,invalues},numeric,output=array([1,10,20,
50,100,200,500,1000]));
      dsol2 :=
      [t, A(t), B(t)]
      [ 1. 0.954237541297251024 0.145762458702748954 ]
      [10. 0.665832112872106862 0.434167887127893281 ]
      [20. 0.507982314965579328 0.592017685034420982 ]
      [50. 0.381561119707259366 0.718438880292740834 ]
      [100. 0.367016860823496994 0.732983139176502818 ]
      [200. 0.366666830014558354 0.733333169985442401 ]
      [500. 0.366666617033504116 0.733333382966496417 ]
      [1000. 0.366666860183484712 0.733333139816515600 ]

```

Fig 3.10. Numerical solution of the direct kinetic problem using Mathcad tools

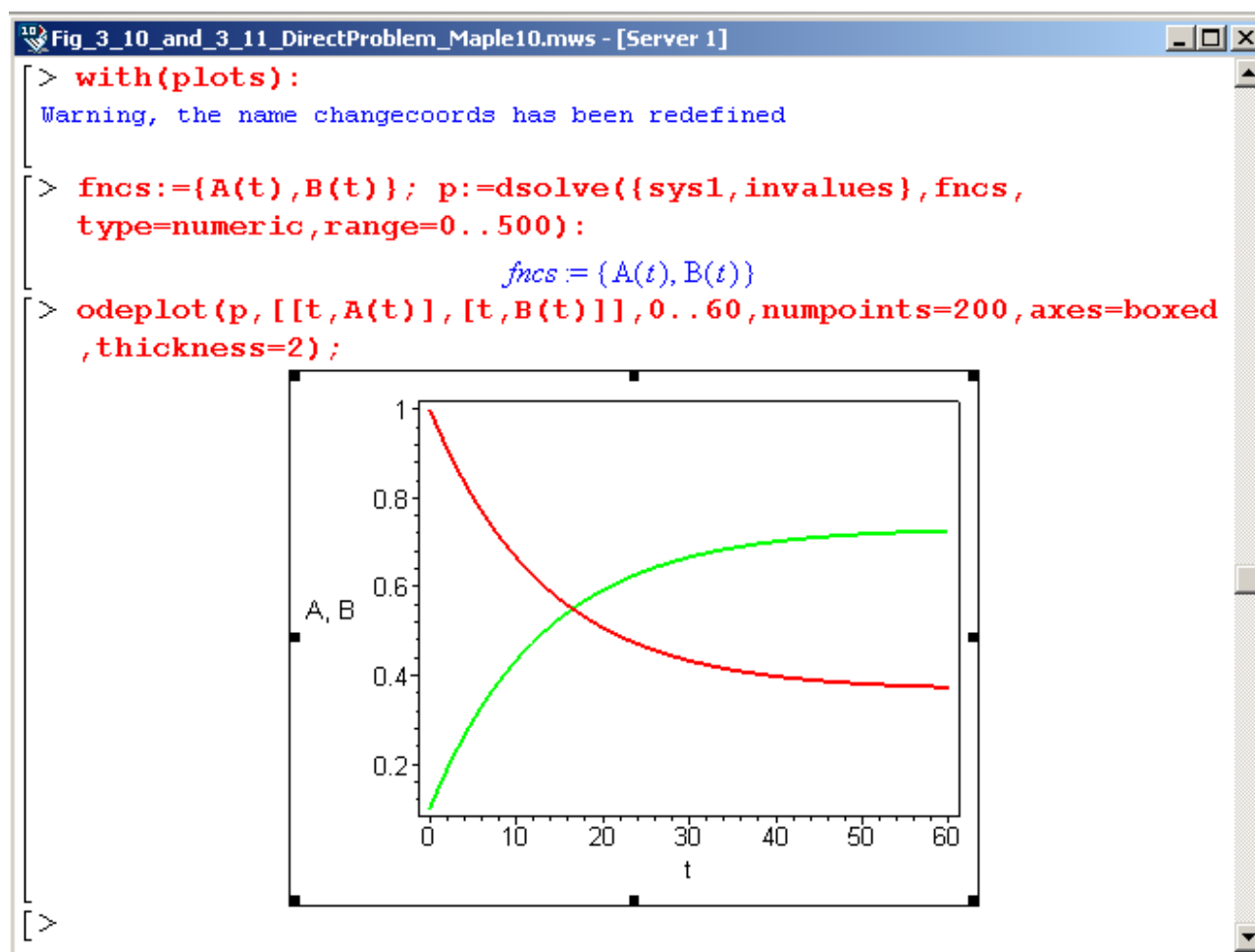


Fig 3.11. Kinetic curves for reversible reaction participants calculated using numerical calculation results

3.4. Oscillation processes modeling

In some reactions, one can see the periodic changes of the reagent concentrations over time. Correspondingly, the rate of the reaction has an oscillating character. Such reactions are called *oscillating* or *periodic*. Nowadays several dozens of homogeneous and heterogeneous oscillating reactions have been explored. Investigations of the kinetic models for these complex processes have allowed formulating a series of general conditions, which are required for the stable oscillations of the reaction rates and intermediate concentrations:

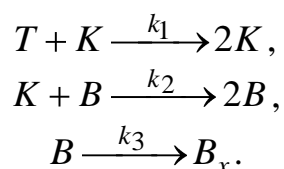
- Stable oscillations appear usually in open systems, where reagent concentrations can be maintained constant.
- The complex reaction must include autocatalytic steps as well as product-inhibited ones;
- The reaction mechanism must include steps with the order higher than first.

These conditions are required but not sufficient for the oscillation to occur in the system. An important role is played also by the ratio between the rate constants of certain steps and starting reagent concentrations. An investigation of the oscillating reactions is still an important chemical kinetics problem because it is crucial in

understanding catalysis, periodic process laws for living systems, and chemical technology.

Sometimes chemical problems can be answered using the knowledge from other sciences that are not related to chemistry at first sight. For example, some information about a complex reactions flow can be gained from the mathematical models of the interspecific competition. A classical example is the “predator–prey” model, which describes the population trends for predators and prey in living conditions (the *Lotka–Volterra* model). The analogies between this model and many reaction schemes are evident.

The main point of the model is the following. Let’s consider some closed ecological system that includes two populations: “predators” and herbivorous “prey”. The population sizes are K and B correspondingly. The prey population is reproduced by means of nutrition. The prey consume grass only. The amount of grass is characterized by the T values. Predators eat solely the prey. Their population trend is determined by the amount of herbivores. There are no natural enemies for the predators. Instead, the latter experience the natural loss (diseases, age-specific death). Thereby, the conditions can be expressed with the following scheme:



Here B_x corresponds to the number of dead predators. Using chemical terminology, one can say that the resulting process is a conversion of the starting reagent T into the product B_x . The process is accompanied by the formation of intermediates K and B , which serve for different kinetic functions.

The stages of population expansion are autocatalytic with the reproduction factors (rate constants) k_1 and k_2 , but the presence of predator mortality (k_3) prevents the unlimited growth of both populations. Undoubtedly, the overall kinetics of the process is affected by the amount of grass necessary for the prey population increase. Assume that we have an unlimited amount of grass, i.e. $T(t)=\text{const}$. Then, based on the given conditions, one can write the following differential equation set:

$$\begin{aligned} \frac{dK}{dt} &= k_1TK - k_2KB = kK - k_2KB, \\ \frac{dB}{dt} &= k_2KB - k_3B. \end{aligned}$$

If the constants for each step and initial population sizes are given, then the numerical solution will allow one to predict prey and predator population trends (fig. 3.12).

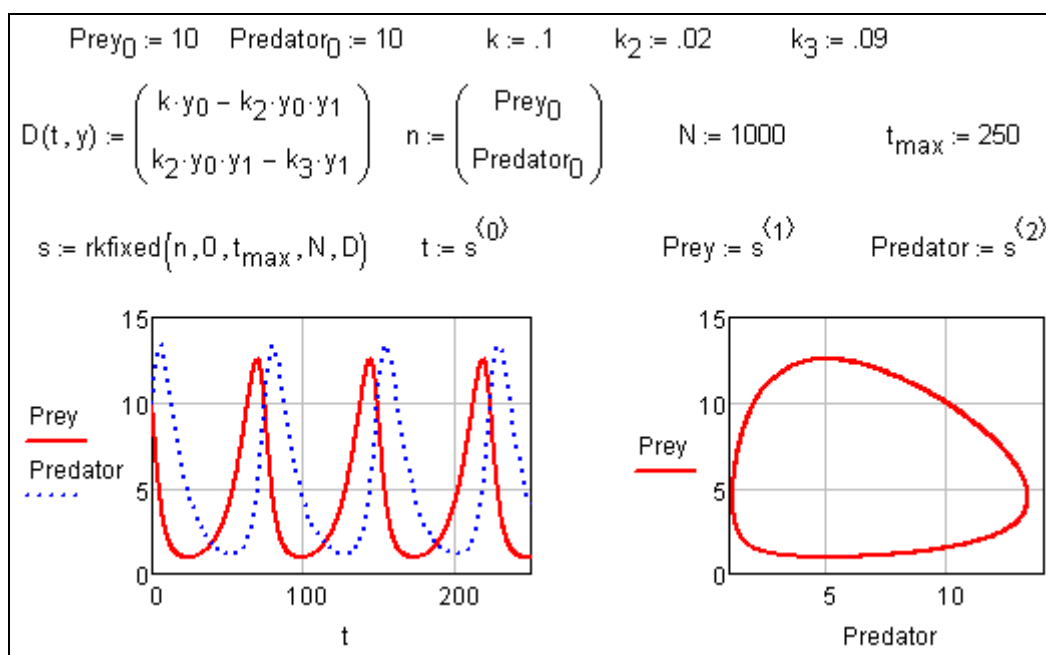


Fig. 3.12. Population trends for predators (dashed line) and prey (solid line) in the Lotka–Volterra model

As fig. 3.12 shows, the population trends for both populations exhibit a continuous wave pattern. For the given initial conditions these oscillations have a constant period and amplitude. There is an interdependence between the two population sizes: increase of one of them impedes the growth of other. In the case of some chemical process described by the Lotka-Volterra model, the concentrations of the intermediates K and B would be oscillating.

Often it is more convenient to present the solutions of such systems not as the “concentration over time” trends but rather as the dependence of one of the concentration on the other. In the second part of fig. 3.12, we have shown the prey population as a function of the predator population — the so called “phase path”. The population dynamics can be represented as a movement along the phase path. The position of the point corresponds to the population sizes at a given moment of time. One can see that the phase path for these initial conditions is a closed graph. In the case of continuous oscillations, the point follows the phase path repeatedly.

Now let’s change the form of the Lotka-Volterra model by dividing both parts of the equations by k_2 , and assuming that $k_2 dt = d\tau$, $k/k_2 = a$, $k_3/k_2 = b$:

$$\frac{dX}{d\tau} = aX - XY,$$

$$\frac{dY}{d\tau} = XY - bY.$$

The system has only two parameters now, a and b . Both of them are positive according to the physical meaning. If one solves the resulting system for a number of initial conditions, he will end up with a phase path set called the **phase portrait** of the system. For the given case we will have the phase portrait as a set of closed

concentric graphs (fig. 3.13). Due to the $a > 0, b > 0$ conditions, all the phase paths are situated in the first quadrant of the coordinate plane. The oscillations occur near some stationary point, which can be determined by putting dX/dt and dY/dt equal to zero. One can easily find that $X_{st} = b, Y_{st} = a$. The corresponding point $(X_{st}; Y_{st})$ is called the **critical point** of the system.

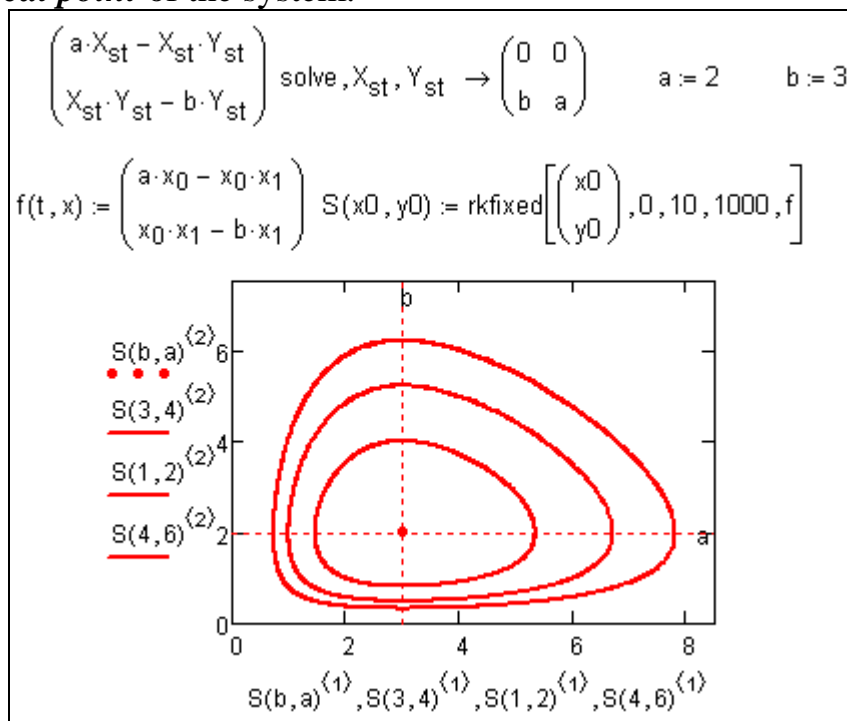


Fig. 3.13. Phase portrait of the Lotka—Volterra system with a critical point

In the case when all the phase paths are closed and “incapsulated” one into the other, the critical point is called a **center**.

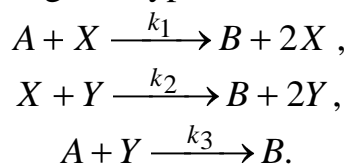
If the initial grass-eater and predator populations equal b and a correspondingly, the simulation will not reveal oscillations in the system. Any deviation from the stationary values will lead to oscillations.

Even though the “predator–prey” model is rather idealized, many kinetic models for real chemical systems are based on it. For example, *D.A.Frank–Kamenetsky* used the Lotka-Volterra model to explain the processes of higher hydrocarbon oxidation.

The hydrocarbon oxidation kinetics is extremely complex because it includes many consequent-parallel steps. Thus, the full mechanism description is problematic. In such cases researchers confine themselves to model descriptions. Each of the model steps may represent a series of elementary stages, and each of the model symbols may correspond to a whole set of compounds playing the same kinetic function.

For example, in the case of a continuous supply of a gasoline–air mixture into the reactor (heated to certain temperature), one can see periodical flashes of the cold flame appearing with a constant frequency. In this case the full combustion does not occur. The oxidation products include aldehydes, organic peroxides and other compounds. Some regularities have been established for this process. In particular,

the flash frequency increases with the increase of oxygen concentration and temperature. In order to explain this effect, D.A.Frank–Kamenetsky suggested the following kinetic scheme involving two types of intermediates, X and Y :



Here A is the starting compound, B is the product, X is the superoxide type molecules or radicals, and Y means the aldehyde type molecules or radicals. One can see that the scheme postulates an autocatalysis with the two intermediates. Let's assume the reagent concentration does not depend on time ($A=\text{const}$), i.e. its consumption rate is compensated by its insertion into the reactor. That will give us the following equation set:

$$\begin{aligned} \frac{dX}{dt} &= k_1 A X - k_2 X Y, \\ \frac{dY}{dt} &= k_2 X Y - k_3 A Y. \end{aligned}$$

After the division of both equation parts by k_2 we end up with the Lotka-Volterra type set:

$$\begin{aligned} \frac{dX}{d\tau} &= aX - XY, \\ \frac{dY}{d\tau} &= XY - bY, \end{aligned}$$

where $a=k_1A/k_2$, $b=k_3A/k_2$, $k_2dt=d\tau$. It was shown before that the solution for this system has a behavior oscillating in time

Let's show the numerical solution of the Lotka-Volterra model using Maple suite tools (fig. 3.14). Here the DEplot command from the DEtools library was used in addition to the dsolve. In this case, in addition to the integral curves set for the phase paths, the **directional field** is visualized. The directional field is a series of arrows, each of which represents the motion direction along the phase path at the given point. In many cases the directional field increases the clearness of the phase portrait. The directional field can also be plotted using the Maple commands phaseportrait and dfieldplot.

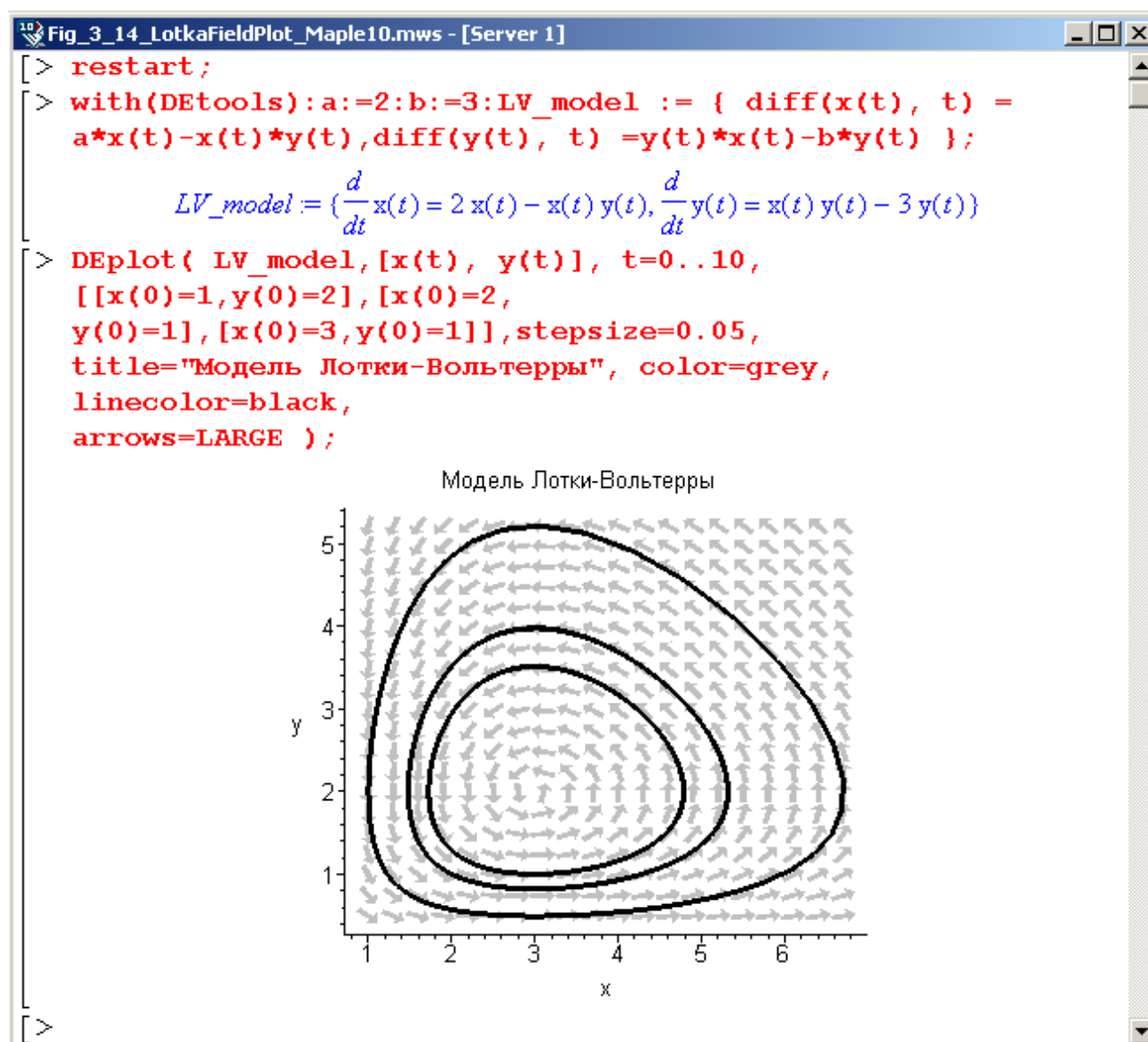
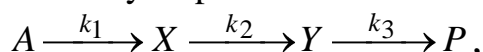


Fig. 3.14. “Predator—prey” model analysis using Maple

To construct the directional field in the Mathcad environment we recommend the user function `field`, which was created by T. Gutman (fig. 3.15).

There are other types of critical points. For example, consider the kinetic scheme consisting of the elementary steps:



in which the first step has the zero order. The concentration changes for the intermediates are described by the equation set:

$$\begin{aligned} \frac{dX}{dt} &= k_1 - k_2 X, \\ \frac{dY}{dt} &= k_2 X - k_3 Y. \end{aligned}$$

Assume $k_1 = 2,0$, $k_2 = 1,0$ and $k_3 = 0,5$. We can plot a series of phase portraits for the different initial concentrations of X and Y based on the numerical solution of the direct kinetic problem (fig. 3.16).

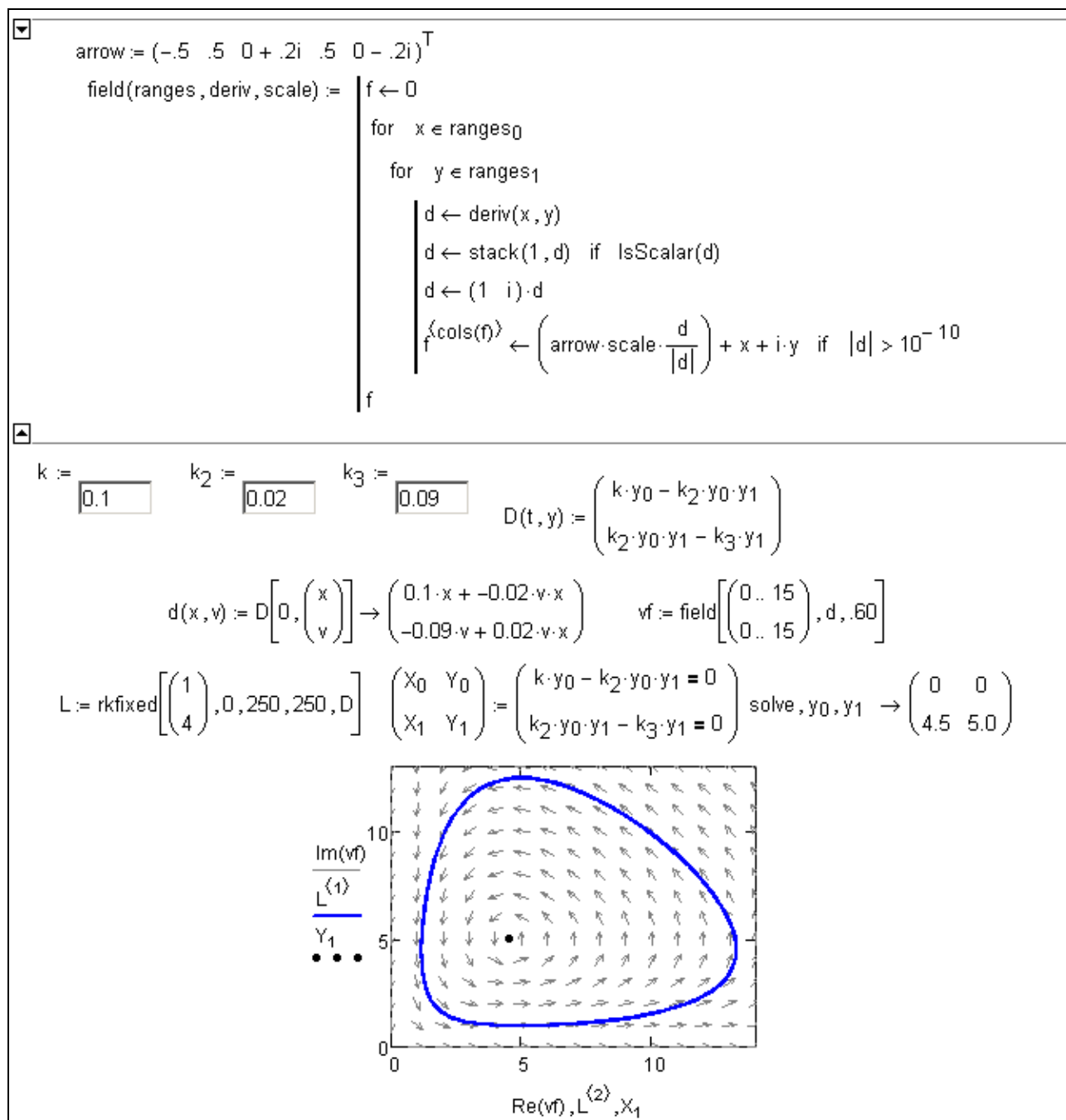


Fig. 3.15. Phase portrait of the Lotka—Volterra system using a directional field

The computation results, presented in fig. 3.16, show that all phase paths converge at one point. Its coordinates are determined by the values of the intermediates stationary concentrations, X_{st} and Y_{st} :

$$\begin{aligned} k_1 - k_2 X_{st} &= 0, \\ k_2 X_{cm} - k_3 Y_{st} &= 0, \end{aligned}$$

which gives $X_{st} = k_1/k_2$, $Y_{st} = k_1/k_3$, or, taking into account the given rate constant values, $X_{st} = 2$, $Y_{st} = 4$. Such type of critical point is called **node**, and oscillations are impossible in this system.

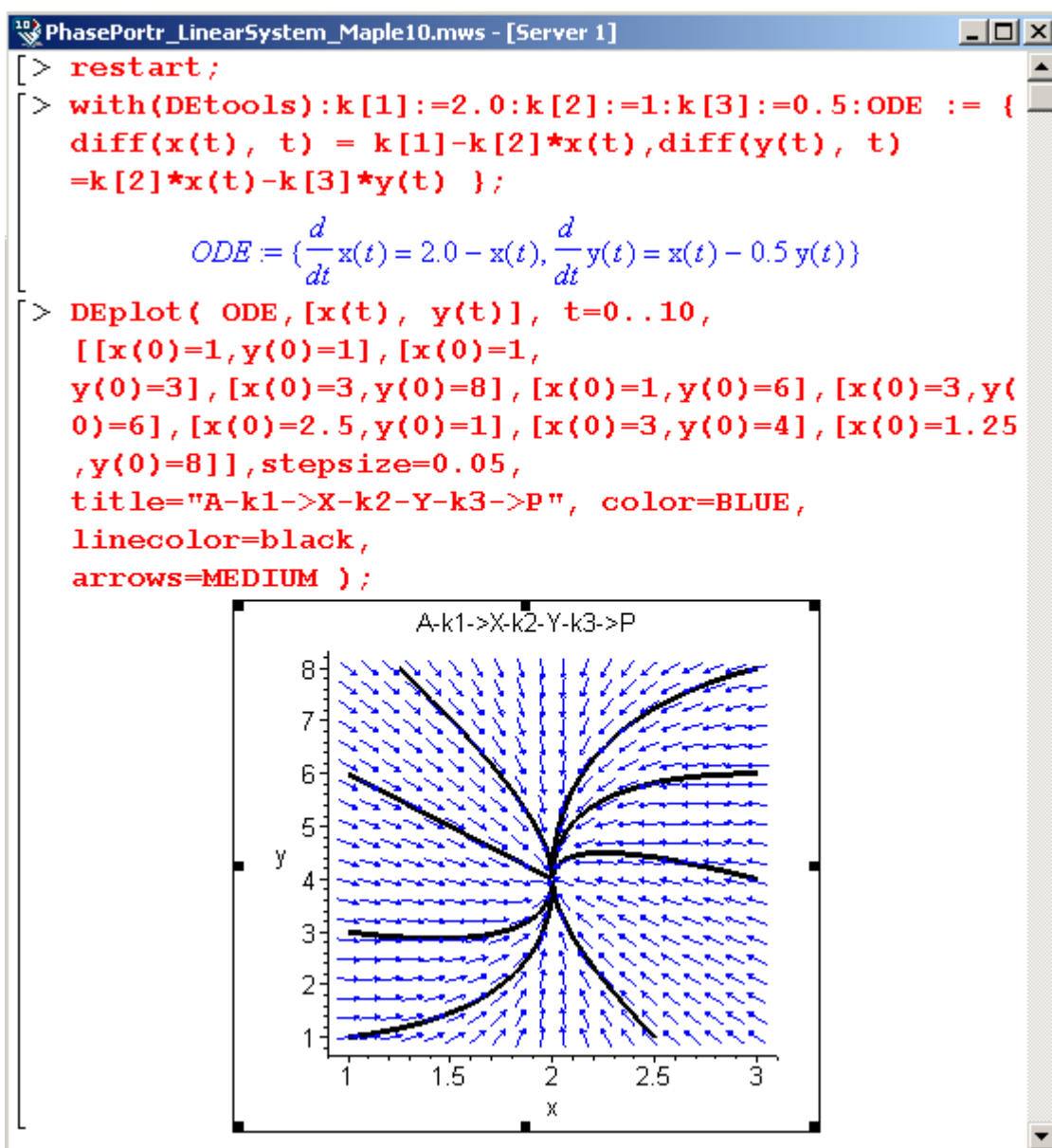


Fig. 3.16. Phase portrait of the system with “node”-type critical point

Now consider the following equation set:

$$\begin{aligned} \frac{dX}{dt} &= aX - bY \\ \frac{dY}{dt} &= aY - bX \end{aligned}$$

This system is also often used in the differential biological models. If one analyzes the corresponding phase portrait with the directional field (fig. 3.17), one can see that all the phase paths approach a critical point and then move away. In this case, we have the “*saddle*” critical point³.

³ In the document shown in fig. 3.17 (as well as some other documents in this chapter) there were used user functions `IntCurves`, `VField` (*T. Gutman*). The reader can find the corresponding documents on the book site.

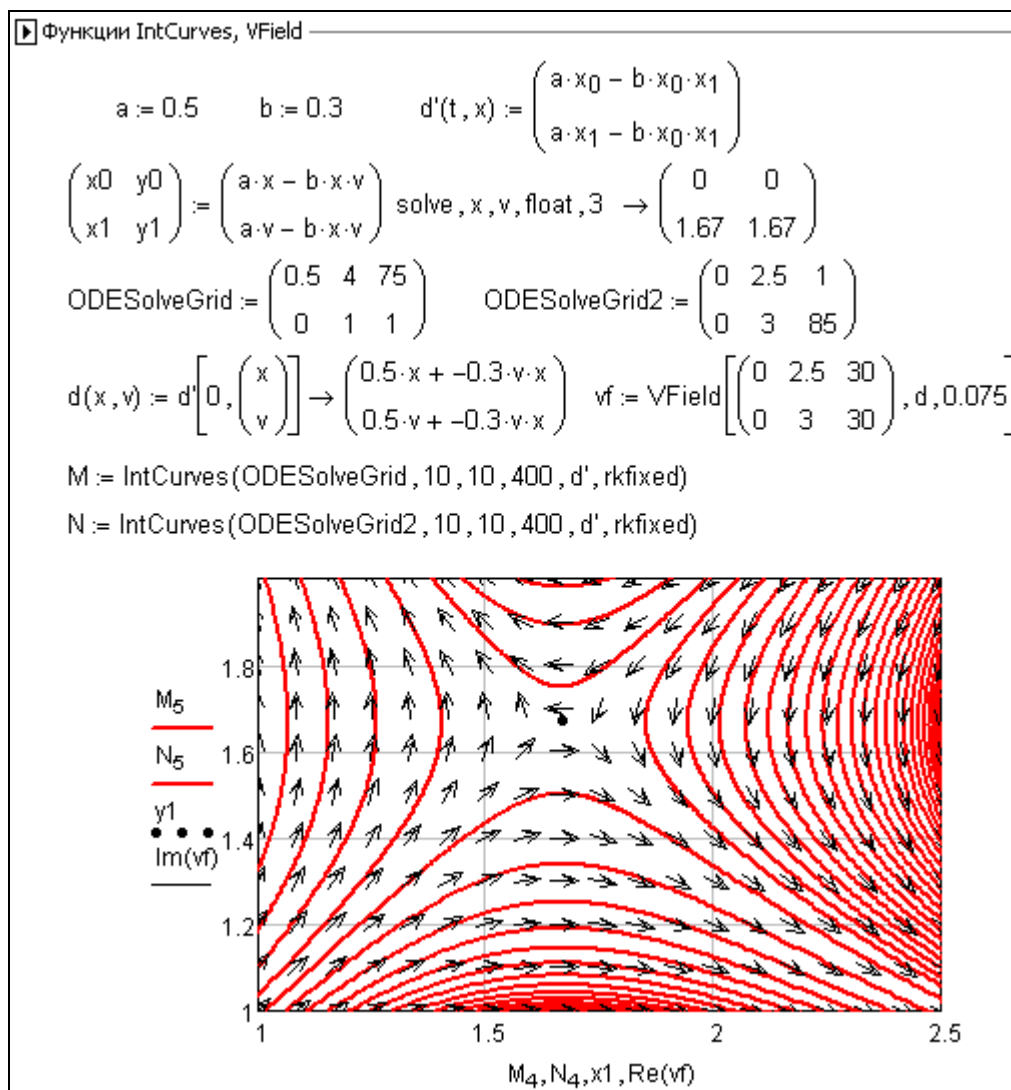
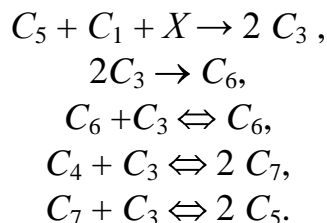


Fig. 3.17. System with a “saddle” critical point

Finally, there is one more remarkable critical point type — *focus*. In order to illustrate it, we will examine one of the kinetic models of photosynthesis.

In the past there was suggested a mechanism for the dark steps cycle of photosynthesis. Sugars with different numbers of carbon atoms, 3 to 7 (trioses, tetroses, pentoses etc.), participate in this cycle. Having labelled the number with a subscript, one can create the scheme of the process:



Here X means triphosphopyridinenucleotide and C_1 is carbon dioxide. This kinetic scheme was analysed by *D.S.Chernavsky*, who assumed some concentrations remaining constant and ended up with the following differential equation set:

$$\frac{dC_3}{dt} = a_1 C_3^2 - a_2 C_3 C_6 + a_0,$$

$$\frac{dC_6}{dt} = b_1 C_3^2 - b_2 C_6^2 - b_3 C_3 C_6.$$

Let's solve the set with Mathcad tools (fig. 3.18), using the numerical integration method with an adaptive step. The constants $a_0, a_1, a_2, b_1, b_2, b_3$ values have been chosen arbitrarily. The results show that there are periodical concentration oscillations, which decay over time.

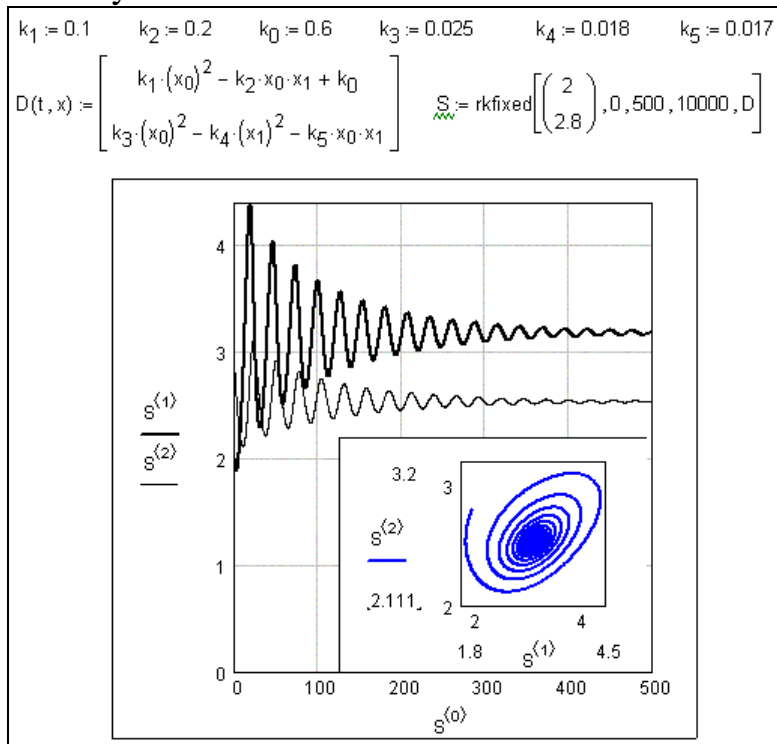


Fig. 3.18. Modelling the photosynthesis kinetics

The phase path is of the spiral form in this case. The spiral “wraps” around a critical point called focus.

The investigation of the critical point character is closely related to the question of the system stability. Here the chemical kinetics borrows some terms from the dynamic system theory, such as *Lyapunov's stability criteria*.

Without a deep discussion of the mathematical apparatus, we will show how the mathematical suites allow one to determine the critical point type. Assume the mathematical model of a process described by a set of two differential equations. In order to find the critical point type one has to:

- ❑ calculate the critical point coordinates on a phase plane. For this one has to solve the corresponding algebraic equation set, which is obtained through the equating of desired functions derivatives to zero;
- ❑ compute the Jacobian matrix for the system using the critical point coordinates;
- ❑ find the eigenvalues λ_1, λ_2 of the latter matrix.

Obtained eigenvalues allow one to establish the critical point type and the stability of the stationary state. Six cases are possible here. They are outlined in fig. 3.19.

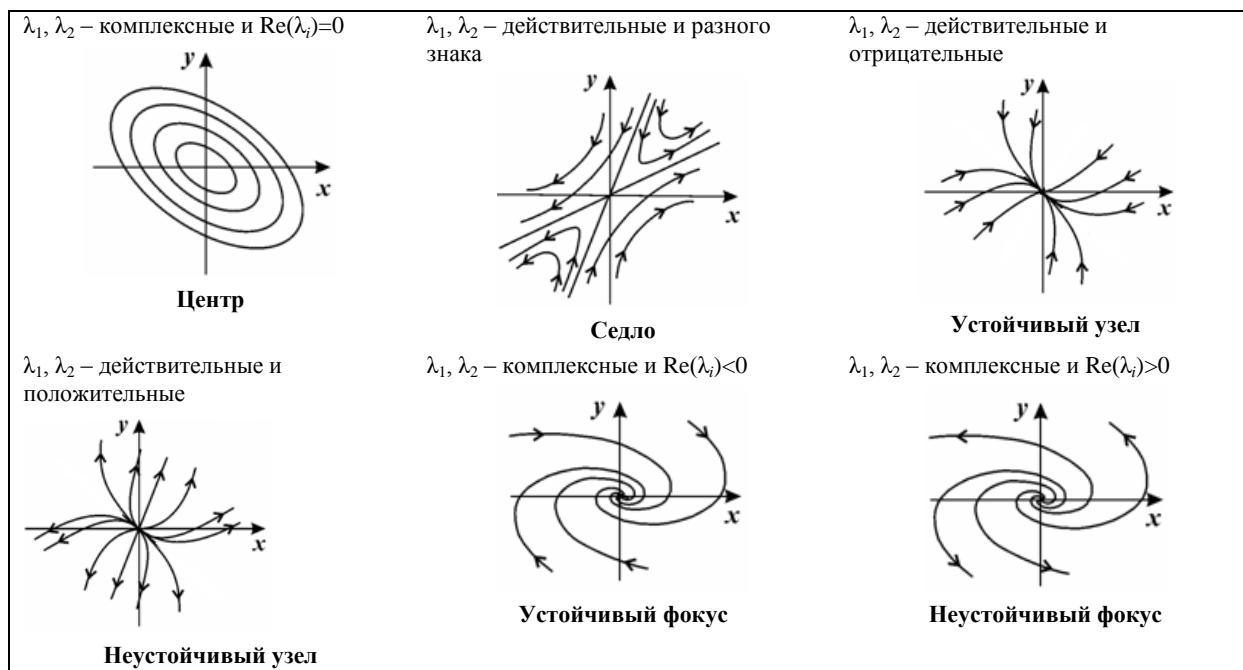


Fig. 3.19. Possible critical point types and phase portraits versus different Jacobian matrix eigenvalues

As an example we will consider the previously discussed microorganism propagation model with slight modifications. Let's assume that the poison produced during the microorganism life can decompose (for example, by means of the Sun's radiation). The poison decomposition will represent an elementary zero-order reaction with the rate constant k_3 . The new mathematical model will look this way:

$$dN / dt = kN - k_1NX .$$

$$dX / dt = k_2N - k_3 .$$

The solution of the direct kinetic problem is shown in fig. 3.20. We can see that in the case of the assumed rate constants the microorganism population is oscillating. The critical point type is the *node*, because all the Jacobian eigenvalues are imaginary.

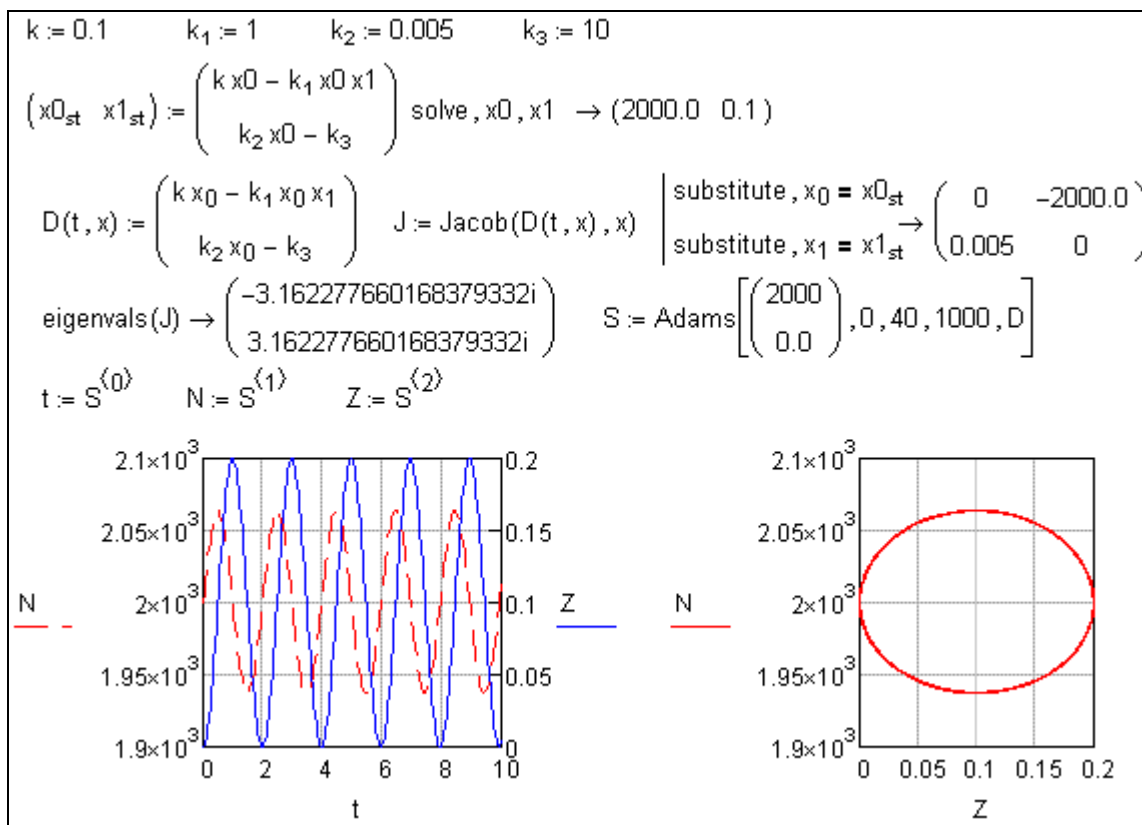
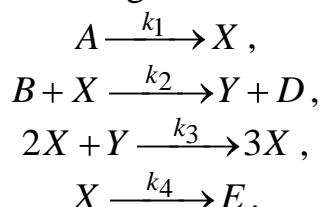


Fig. 3.20. Oscillation mode of the population trend in microorganism colony

The first “chemically grounded” model of a oscillating reaction is a model, which was proposed by I. Prigozhin and is called *bruesselator*. The model is based on a hypothetical reaction with the following mechanism:



It is assumed that the concentrations of the reagents A and B do not change over time. The concentrations of D and E are not included in the mass action law. That is why one need only two equations for the formal kinetic description of the reaction:

$$\begin{aligned}
 \frac{dX}{dt} &= k_1 A - k_2 B X + k_3 X^2 Y - k_4 X \\
 &= k_{1ef} - k_{2ef} X + k_2 X^2 Y - k_4 X \\
 \frac{dY}{dt} &= k_2 B X - k_3 X^2 Y = k_{2ef} X - k_3 X^2 Y.
 \end{aligned}$$

It is possible to reduce the number of the controlling parameters in this system by substituting some variables: $\tau = k_4 t$, $x = \sqrt{k_3/k_4} X$, $y = \sqrt{k_3/k_4} Y$. After these changes the system takes the form:

$$\begin{aligned}
 \frac{dx}{d\tau} &= a - (b+1)x + x^2 y, \\
 \frac{dy}{d\tau} &= bx - x^2 y,
 \end{aligned}$$

where $a = k_{1ef} \sqrt{k_3/k_4^3}$, $b = k_{2ef}/k_4$.

A remarkable feature of the bruesselator is the variety of the critical point types and, consequently, of the phase portraits depending on the a and b parameters ratio (table 3.3).

Table 3.3 – Critical point types for the bruesselator

Parameters a and b ratio	Critical point type
$b < (a-1)^2$	Stable node
$b < a^2+1$	Stable focus
$b = a^2+1$	Center
$b > a^2+1$	Unstable focus (limit cycle)
$b > (a+1)^2$	Unstable node

The case $b > a^2+1$ requires additional examination. The critical point type is the unstable focus. One can see the appearance of the so-called *limit cycle* in the phase portrait. In this case, any point in the phase plane will end up following the same closed phase path regardless of the initial conditions. This means that stable asymptotic concentration oscillations (auto-oscillations) of the same amplitude and frequency will appear with the course of time. Correspondingly, this case is essentially different from the Lotka-Volterra model. In the latter, one can find closed phase paths as well, but there is no the only path that does not depend on the initial conditions. The point set, which “attracts” all phase paths, was called by I. Prigozhin an *attractor*. Thus, the bruesselator has the attractor, while the Lotka-Volterra system does not have. The appearance of the bruesselator limit cycle can be seen in fig. 3.21. The Mathcad tools were used to plot the phase portrait assuming $a=1$, $b=3,25$.

Nowadays many real chemical systems are known, in which processes, accompanied by the concentration oscillations, take place. These can be both heterogeneous and homogeneous reactions. In particular, the hydrogen peroxide reduction on the mercury drop surface can progress periodically in specific conditions. The conjugate process of mercury surface oxidation is accompanied by a change of the surface tension. It leads to the drop shape changes. The oscillating mode of the reaction can be observed through the periodical changes of the mercury drop shape, which resembles a heartbeat (“mercury heart”).

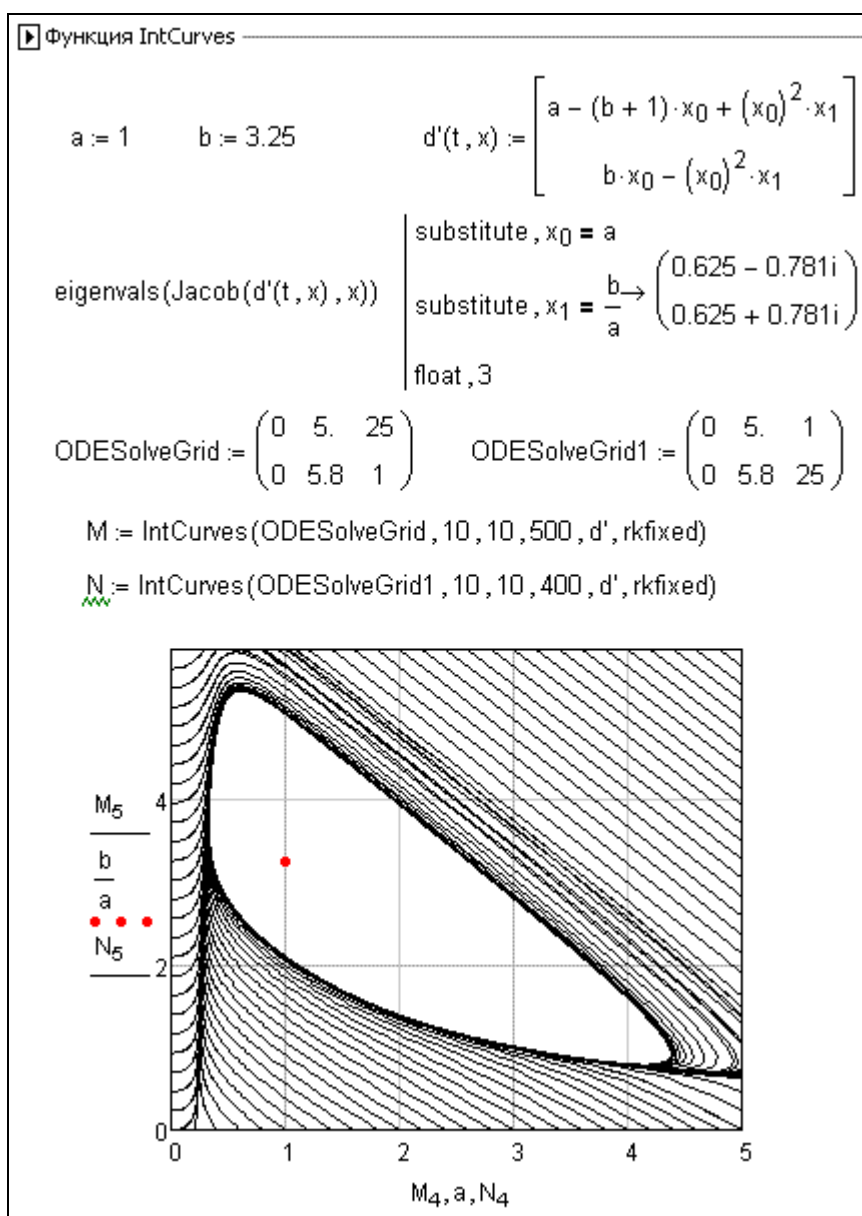


Fig. 3.21. Brusselator phase portrait with a limit cycle

The oscillating reactions in homogeneous aqueous media are of a special interest. Probably, the oxidation of organic acids and their esters by the bromate ion is investigated the most. *B.P. Belousov* (1951) observed the periodic color changes during the oxidation of citric acid by bromate ion in sulfuric acid solution in the presence of cerium ions. The detailed investigation of this process was done by *A.M. Zhabotinsky*. The discovery of this reaction stimulated the investigation of periodical processes in chemical systems. It became evident that homogeneous oscillating reactions underlie the most important biochemical processes: generation of biorhythms and nerve impulses, muscles contraction, etc. As of today, the reaction of catalytic oxidation of different reducing agents by bromic acid ($HBrO_3I$), following the auto-oscillating mode, is called the ***Belousov-Zhabotinsky reaction***. This reaction goes in the acidic water solution and is accompanied by the concentration oscillations for the oxidized and reduced catalyst forms and intermediates. As a catalyst one can use transition metal ions, such as manganese or cerium. The reducing agents can be

different organic compounds (malonic acid, acetylacetone, etc.)

We want to mention that, in spite of many publications dealing with Belousov-Zhabotinsky reaction, the true mechanism of this process is still unknown. Many kinetic schemes were proposed to explain the existence of the concentration oscillations. One of the possible mechanisms is shown in the table 3.4.

Here one can find several important conjugated processes.

1. During the step (1) $HBrO_2$ is formed. It acts as an autocatalyst in the following reactions.

2. The extensive chain reaction of the oxidant BrO_3^- with the autocatalyst provides the conditions for the Me^+ ions oxidation (steps 4—7).

3. The oxidation is inhibited due to the chain termination (step 3).

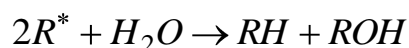
4. The oxidized form of the catalyst is reduced during step 14.

The way other reagents react can be deduced from the given scheme. We have to admit that in spite of the large number of steps, this kinetic model should be considered as simplified. However, the solution of the direct kinetic problem for this scheme at the given conditions (see table 3.4) shows the presence of stable concentration oscillations. A fragment of the corresponding Mathcad document is shown in fig. 3.22. Here the mathematical model was developed in compliance with the kinetic scheme given in the table 3.4. It was assumed that the hydrogen ion concentration is constant during the reaction. One can find the corresponding document on the book's site.

Table 3.4 – Possible mechanism of the Belousov-Zhabotinsky reaction

Nº	Step number	Reaction	Kinetic parameters values
1	1-2	$BrO_3^- + Br^- + 2H^+ \Leftrightarrow HBrO_2 + HOBr$	$k_1=2, 1;$ $k_2=1, 0 \cdot 10^4$
2	3	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$k_3=3, 0 \cdot 10^6$
3	4-5	$BrO_3^- + HBrO_2 + H^+ \Leftrightarrow 2BrO_2^* + H_2O$	$k_4=4, 2 ;$ $k_5=4, 2 \cdot 10^7$
4	6-7	$BrO_2^* + Me^+ + H^+ \Leftrightarrow HBrO_2 + Me^{2+}$	$k_6=8, 0 \cdot 10^4$ $k_7=8, 9 \cdot 10^3$
5	8	$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$	$k_8= 3, 0 \cdot 10^3$
6	9-10	$HOBr + Br^- + H^+ \Leftrightarrow Br_2 + H_2O$	$k_9=8, 0 \cdot 10^9$ $k_{10}=1, 1 \cdot 10^2$
7	11	$RH + Br_2 \rightarrow RBr + Br^- + H^+$	$k_{11}= 4, 6 \cdot 10^3$
8	12	$HOBr + R^* \rightarrow ROH + Br^*$	$k_{12}=$ $1 \cdot 10^6 \dots 1 \cdot 10^7$
9	13	$RH + Br^* \rightarrow Br^- + H^+ + R^*$	$k_{13}=1, 0 \cdot 10^6$
10	14	$RH + Me^{2+} \rightarrow Me^+ + H^+ + R^*$	$k_{14}=2, 0 \cdot 10^{-1}$

11 15



$$k_{15} = 3,20 \cdot 10^9$$

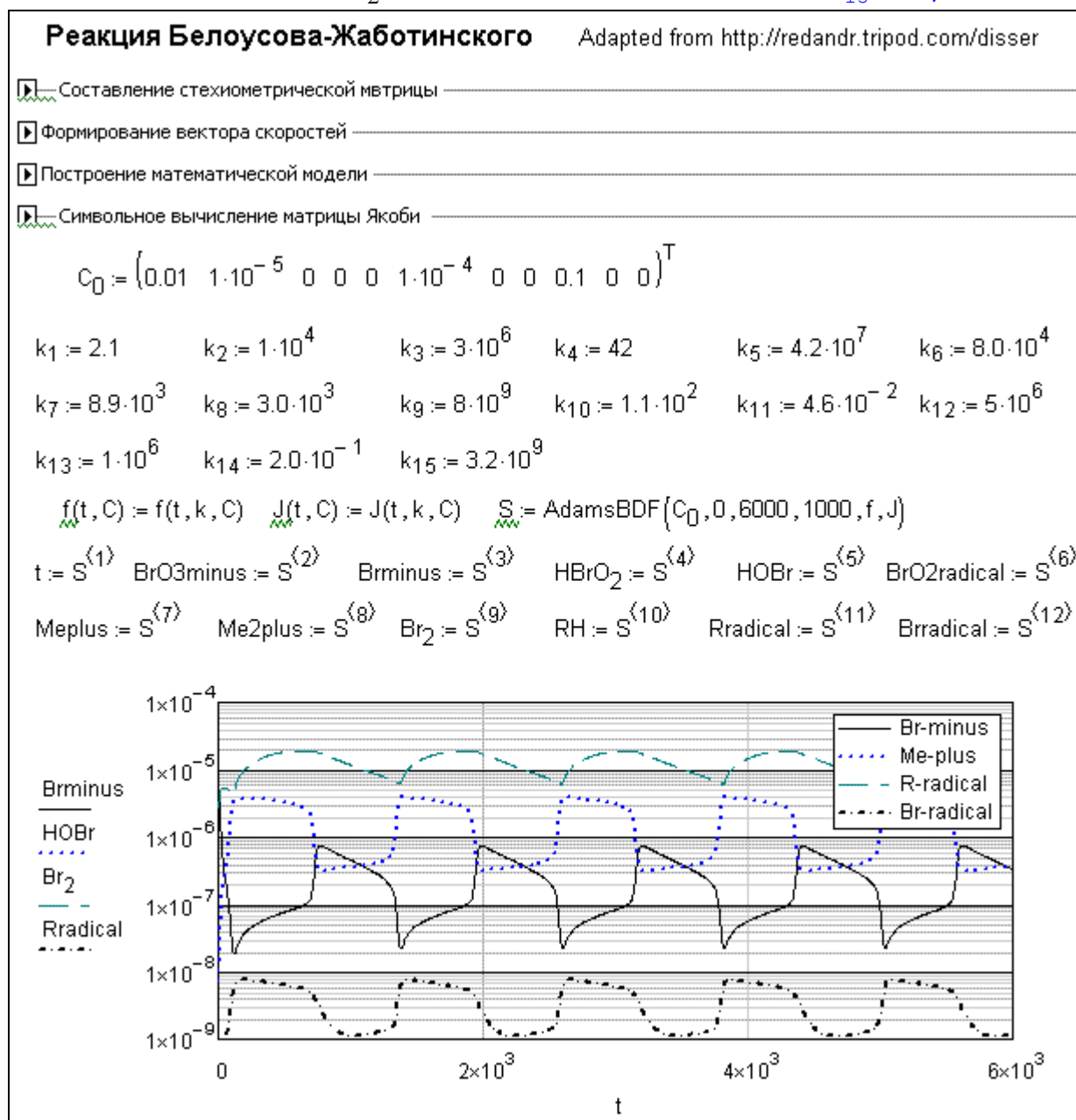
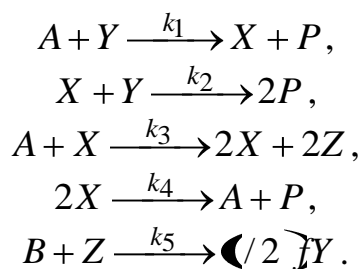


Fig. 3.22. Concentration oscillations in the Belousov–Zhabotinsky reaction

Somewhat different scheme for the Belousov-Zhabotinsky reaction was suggested by Field, Korös and Noyes. The model is called *oregonator*. It includes following stages:



Here A corresponds to the BrO_3^- ion; B corresponds to all organic reagents that can be oxidized; P is $HOBr$; X is $HBrO_2$; Y is the Br^- ion; Z is the reduced form of

the catalyst. The mathematical model can be written as a set of three differential equations:

$$\begin{aligned}\frac{dX}{dt} &= k_1AY - k_2XY + k_3AX - 2k_4X^2, \\ \frac{dY}{dt} &= -k_1AY - k_2XY + \frac{1}{2}fk_5BZ, \\ \frac{dZ}{dt} &= 2k_3AX - k_5BZ.\end{aligned}$$

It is assumed that the concentrations of the compounds A and B remain constant during the reaction. By using dimensionless variables, one can transform the set:

$$\begin{aligned}\frac{dx}{d\tau} &= \frac{qy - x - y + x[1 - x]}{\varepsilon}, \\ \frac{dy}{d\tau} &= \frac{-qy - x - y + fz}{\varepsilon'}, \\ \frac{dz}{d\tau} &= x - z,\end{aligned}$$

where $x = \frac{2k_4}{k_5A}X$; $y = \frac{k_2}{k_5A}Y$; $z = \frac{k_4k_5B}{k_3A^2}Z$; $\tau = k_5Bt$. Now the model has three controlling parameters:

$$\varepsilon = \frac{k_5B}{k_3A}, \quad \varepsilon' = \frac{2k_4k_5}{k_2k_3A}, \quad q = \frac{2k_1k_4}{k_2k_3},$$

values of which influence greatly the system dynamic behavior.

The document shown in fig. 3.23 can be used as a template in the computer modeling of the oregonator model. By changing the controlling parameters, one can see a variety of the reaction modes with different amplitudes and oscillation frequencies, an appearance of limit cycles, changes in phase paths trajectories, etc. The value of the stoichiometric factor f is also of great importance. Compared to bruesselator, this model is more complex in analysis of possible stationary states and plotting of the phase portraits. The reader can find more details in the specialized literature.

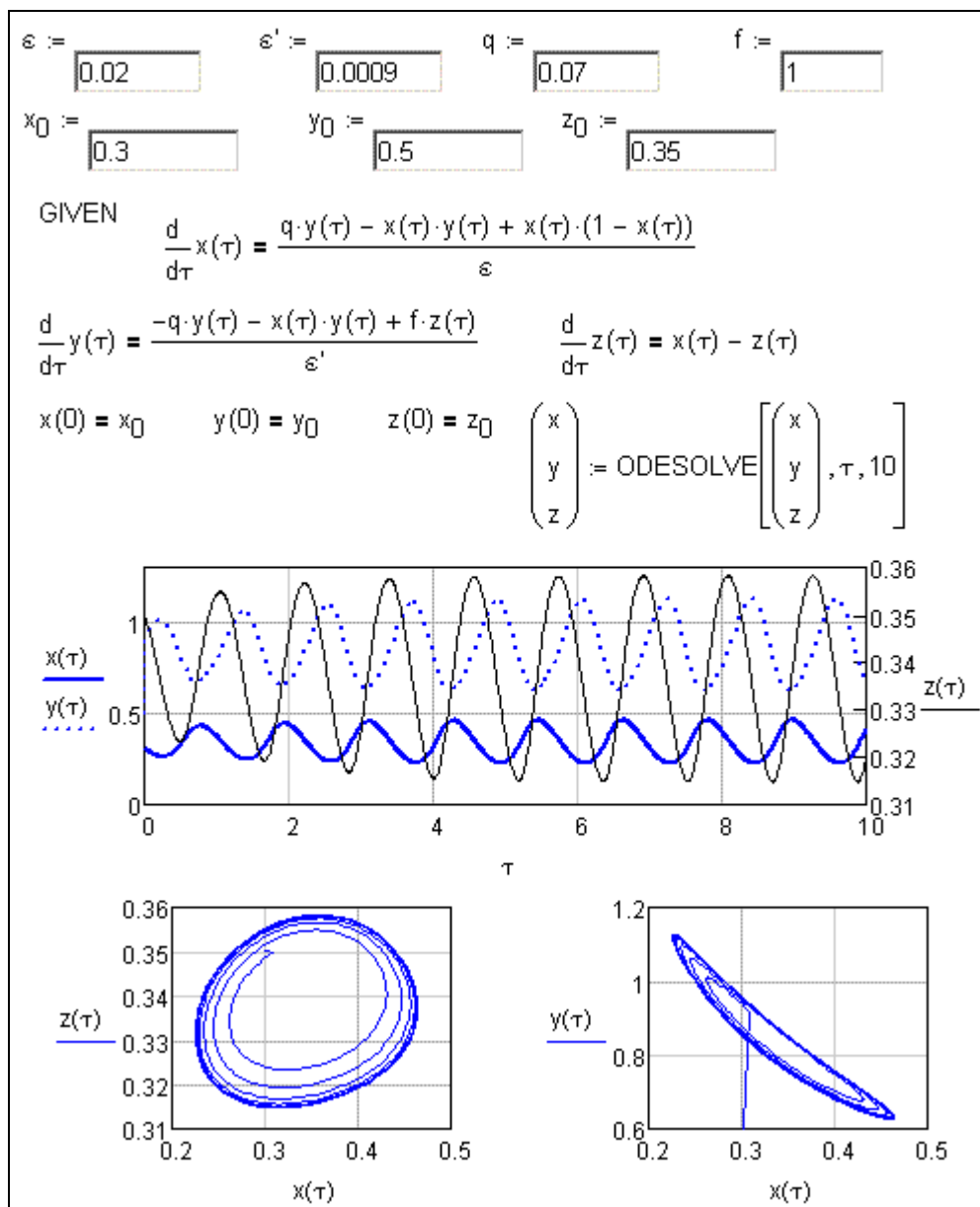


Fig. 3.23. One of the direct problem solutions for the Oregonator problem

3.5. Some points on non-isothermal kinetics

By this point, we were considering only the chemical kinetics problems in case of constant temperature of the reaction mixture. But the temperature can change due to ambient conditions (forced heating or cooling) as well as due to internal factors (heat liberation or adsorption during reaction). Previously discussed methods are not sufficient in this case. The mathematical model of the reaction becomes complicated because the temperature is now a function of time. While equations describing a material balance of the system are sufficient for isothermic kinetics, in case of altering temperature one has to consider energy balance as well.

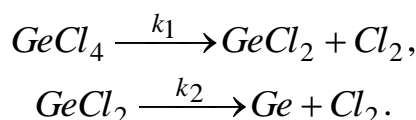
If the reaction has a thermal activation character, changes in temperature lead to changes in the rate constant. This relationship is often described by the Arrhenius equation:

$$k = k_0 e^{-\frac{E_a}{RT}},$$

where E_a is the activation energy (J/mol), k_0 is the pre-exponential factor. The Arrhenius equation is based on the *collision theory*. The theory exploits ideas of an energy barrier and effective collisions of the reacting particles, which happen in a unit of space over a unit of time. The k_0 value is proportional to the total collision number. The activation energy determines the energetic conditions for an active collision — the collision when a transformation of the reagents into the products is possible. It is a certain excess of energy in comparison with the average reactants energy, which have to be applied for the reacting species to react. The Arrhenius equation implies that the reaction rate increases when the temperature rises. The smaller the activation energy is, the greater such increase will be.

So, the rate constant depends on temperature. In the case of the altering temperature the rate constant also becomes a function of time. Consequently, when solving the direct kinetics problem, we have to add the corresponding equations (the temperature over time relationships) to the reaction model.

Let's consider one of the non-isothermic kinetics cases. Some amount of germanium (IV) chloride is being heated. The heating is accompanied by a consequent decomposition:



Assume the heat exchange is organized in a way that the heating appears with a constant rate $\gamma = 10 \text{ K/min}$. One is asked to establish how the gross mass of solids will change if 0.002 mol of GeCl_4 is being heated. The initial temperature is 298 K . It is known that the Arrhenius' relationships for the rate constants have the following form:

$$k_1(T) = 3 \cdot 10^{12} e^{-\frac{29000}{RT}}, \quad k_2(T) = 6 \cdot 10^{14} e^{-\frac{48000}{RT}}.$$

In these equations the pre-exponential factors have dimensions of min^{-1} , activation energies are given in cal/mol .

A mathematical model of the process consists of three differential equations that describe the changes in reactant amounts:

$$\begin{aligned} \frac{dn_{\text{GeCl}_4}}{dt} &= -k_1 n_{\text{GeCl}_4} = -3 \cdot 10^{12} \exp\left[-\frac{29000}{R(t_0 + \gamma t)}\right] n_{\text{GeCl}_4}, \\ \frac{dn_{\text{GeCl}_2}}{dt} &= k_1 n_{\text{GeCl}_4} - k_2 n_{\text{GeCl}_2} = 3 \cdot 10^{12} \exp\left[-\frac{29000}{R(t_0 + \gamma t)}\right] n_{\text{GeCl}_4} \\ &\quad - 6 \cdot 10^{14} \exp\left[-\frac{48000}{R(t_0 + \gamma t)}\right] n_{\text{GeCl}_2}, \\ \frac{dn_{\text{Ge}}}{dt} &= k_2 n_{\text{GeCl}_2} = 6 \cdot 10^{14} \exp\left[-\frac{48000}{R(t_0 + \gamma t)}\right] n_{\text{GeCl}_2}, \end{aligned}$$

as well as of a heating rate equation:

$$\frac{dT}{dt} = \gamma.$$

Initial conditions for the given ODE set are: $n_{GeCl_4} = 0,002$; $n_{GeCl_2} = 0$; $n_{Ge} = 0$; $T = 298$.

To integrate this ODE set one can use any of the previously discussed mathematical suite built-in tools. In fig. 3.24 we have shown how to solve the problem using the Mathcad built-in function `AdamsBDF`. The plots allow one to track the trends of compound concentrations over time. As one can see, during the first 15 mins of heating the amount of the starting material virtually remains constant. After that, decomposition occurs with a notable rate. When $GeCl_4$ has decomposed, the solid phase of the reaction mixture consists solely of $GeCl_2$. This composition remains unchanged until approximately the 30th minute of heating, when the intermediate begins to decompose into the final product. Finally, some time later the mixture will consist of pure germanium. One can track the change in mass of the initial sample in the same way.

When describing the processes of non-isothermic kinetics, it is convenient to use a unitless variable — conversion of the starting compound X . For example, if we have a single first-order reaction under the programmed temperature changes conditions, we can describe its kinetics with a set of two equations:

$$\frac{dX}{dt} = k_0 e^{-E_a/RT} [1 - X] \quad \frac{dT}{dt} = \gamma.$$

with initial conditions $X = 0$, $T = T_0$. The numerical solution of this set for given kinetic parameters values and linear heating mode (fig. 3.24) shows that a conversion vs. time plot has a distinct S-shape. A slope of such a curve changes depending on the given temperature change rate. It important to note that such curve can be obtained experimentally with a special device called derivatograph. Information about the system behavior within a given temperature range is completely enough for solving the inverse problem, i.e. for the determination of the reaction kinetic parameters using experimental data.

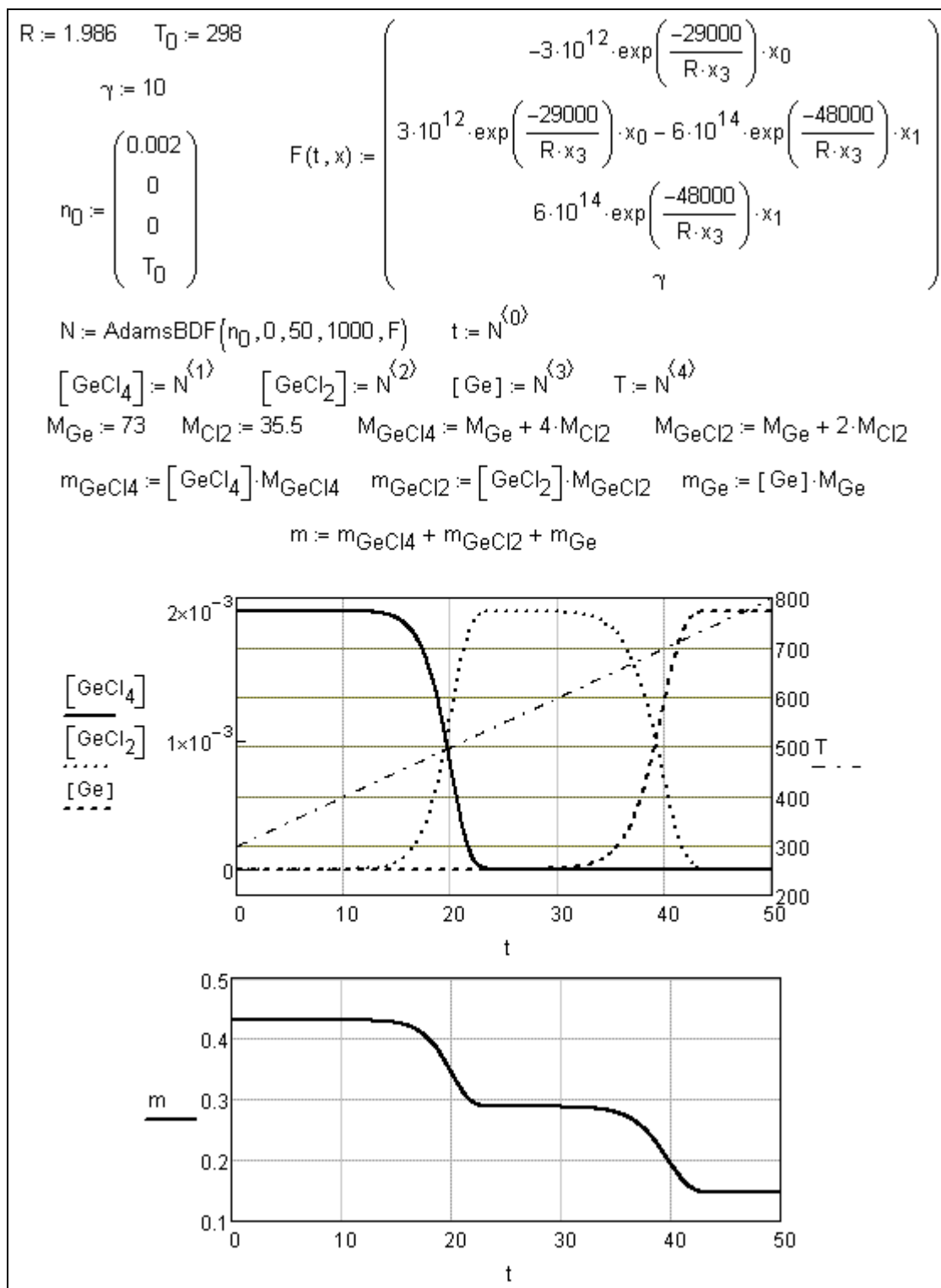


Fig. 3.24. Solution of the $GeCl_4$ decomposition problem

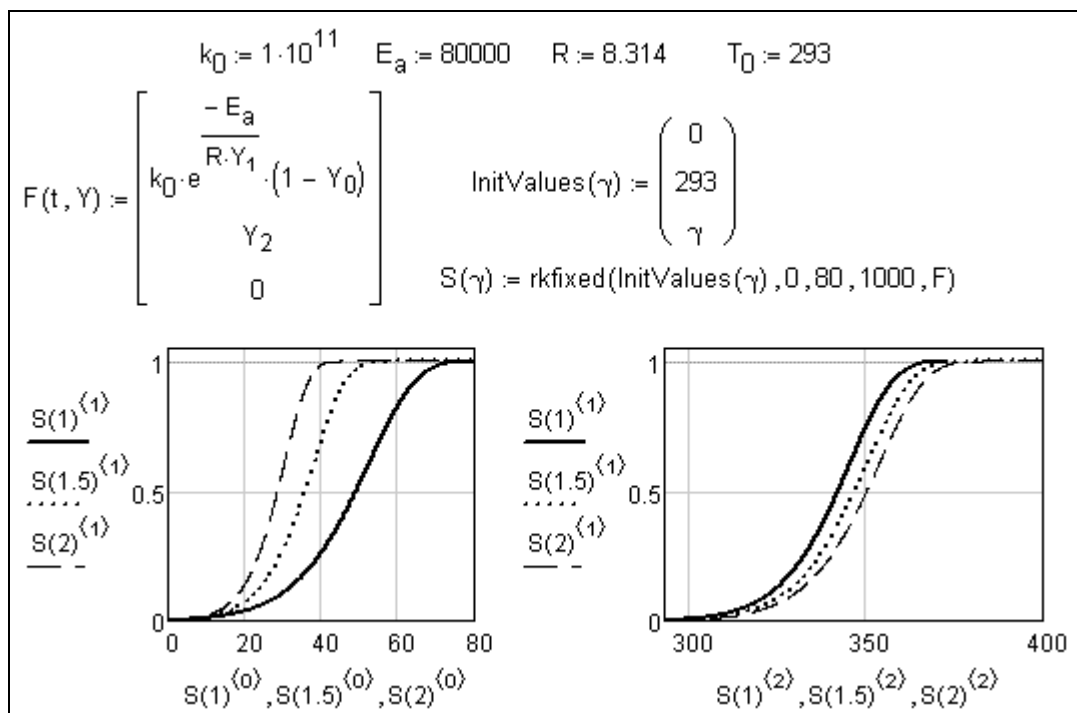


Fig. 3.25. Conversion vs. time and temperature for different heating rates

We want to point out that so far we considered only the cases when the temperature changes were controlled by external factors (i.e. was determined by the experiment conditions).

If an exothermic reaction takes place in an isolated system, in other words, when the heat exchange with environment is absent (adiabatic reactor), a temperature will apparently increase over time. The rate of this increase depends both on the kinetic parameters (rate constant) and on the thermodynamic properties of the system (thermal conditions of the reaction, heat capacity). For a well-mixed periodic reactor, where a single first-order reaction $A \rightarrow B$ occurs, the mathematical model is described by this set of equations:

$$r_A \mathbf{C} = k_0 e^{-E_a / RT} \mathbf{C}_A \mathbf{C},$$

$$\frac{dC_A \mathbf{C}}{dt} = -r_A \mathbf{C},$$

$$\rho C_p \frac{dT \mathbf{C}}{dt} = \Delta H r_A \mathbf{C}.$$

Here ρ is density, kg/m^3 , and C_p is specific heat capacity of the reaction mixture, $J/(kg \cdot K)$. ΔH is the reaction heat effect (taking the sign into account), J/mol . To be specific, these parameters depend on temperature. In addition, heat capacity and density can change as the reaction goes. One should account for that when performing important calculations. In order not to overcomplicate, we assume that these values are constant. We will define an additional parameter: $J = \Delta H / \rho C_p$.

One can see that

$$\frac{dT \mathbf{C}}{dt} = -J \frac{dC_A \mathbf{C}}{dt},$$

An integration of this equation with the initial conditions $T(0)=T_0$, $C_A \stackrel{\circ}{=} C_{A0}$ gives:

$$T - T_0 = J(C_{A0} - C_A)$$

In the case of adiabatic conditions, the system will warm up and reach the final temperature that corresponds to an exhaustion of the reagent:

$$T_{ad} = T_0 + JC_{A0}$$

The temperature T_{ad} is called **adiabatic temperature**.

The modeling results for the behavior of this system are shown in fig. 3.26. The initial parameters were: $k_0=1 \cdot 10^5 \text{ s}^{-1}$, $E_T=E_a/R=5000 \text{ K}$, $C_{A0}=1 \text{ kmol/m}^3$, $J=100 \text{ K} \cdot \text{m}^3/\text{kmol}$. The reader can see that performing the calculations is rather simple.

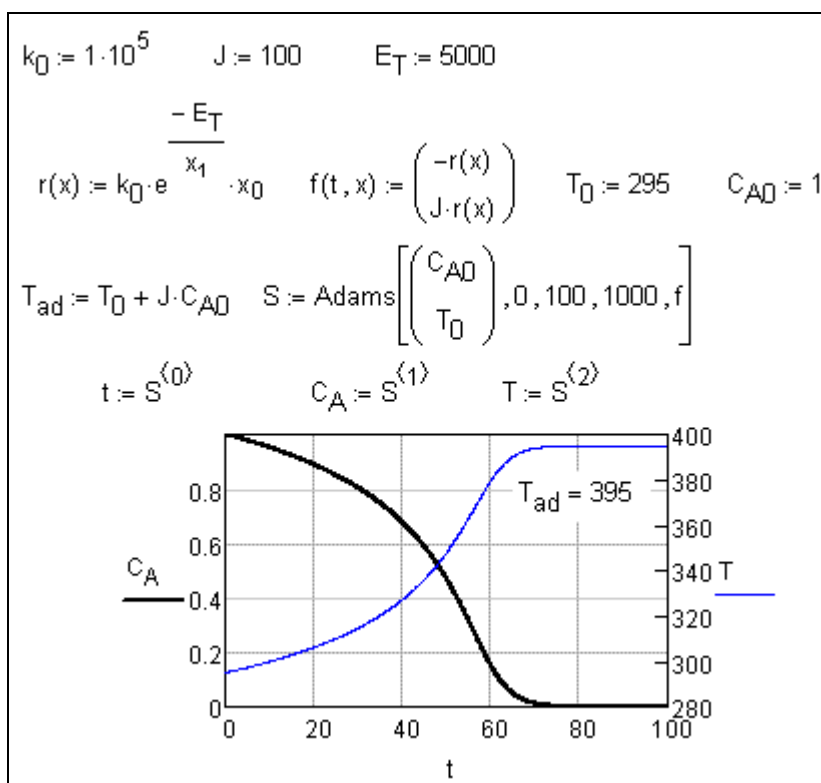


Fig. 3.26. Temperature and reagent concentration changes in a periodic adiabatic reactor

In the real conditions, some heat from the reaction is liberated into environment through the reactor walls. A differential equation for the temperature changes is given in the following form in this case:

$$\frac{dT}{dt} = Jr_A + \frac{hS(T_s - T)}{\rho C_p V}$$

In order to follow operational trends of such non-adiabatic reactor, one have to introduce additional parameters: heat transfer coefficient h , $W/(m^2 \cdot K)$, reactor volume V , m^3 , wall surface S , m^2 . In fig. 3.27 one possible way to compute the reagent concentration and reaction mixture temperature as a function time is shown.

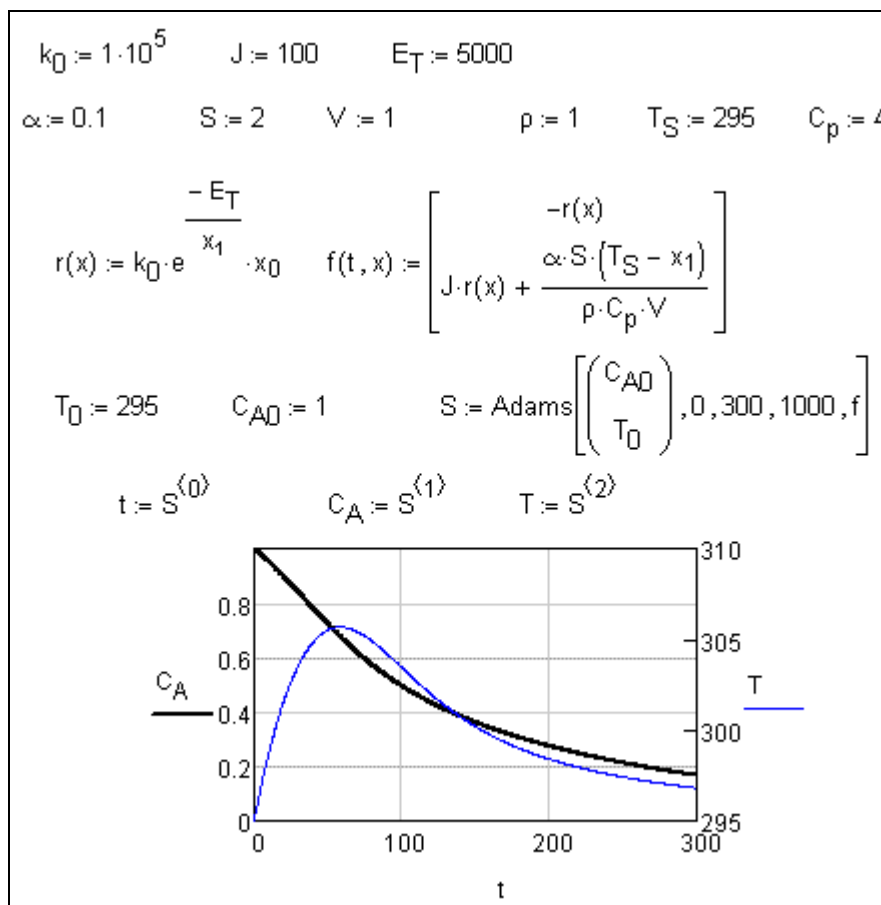


Fig. 3.27. Operation dynamics of a periodic nonadiabatic reactor

For a well-mixed flow reactor working in an adiabatic mode:

$$\frac{dC_A}{dt} = \frac{C_{A0} - C_A}{\tau} - r_A$$

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + J r_A$$

Here τ is, and T_0 is the reagent temperature when entering the reactor. The solution of Cauchy problem for this reactor type allows one to conclude: the dynamic portrait can change strikingly depending on temperature of the initial mixture. Such situation is illustrated on fig. 3.28. One can see that for the time $\tau=60$ s many different kinetic curves as well as temperature—time relationships are possible, even though the initial temperatures differ only for 1 K. In both cases a stationary state is reached. However, for $T_0 = 274$ K the stationary conversion is low and does not exceed 18%. If the initial temperature equals 275 K, other stationary state is reached. The latter corresponds to rather high conversion (>84%).

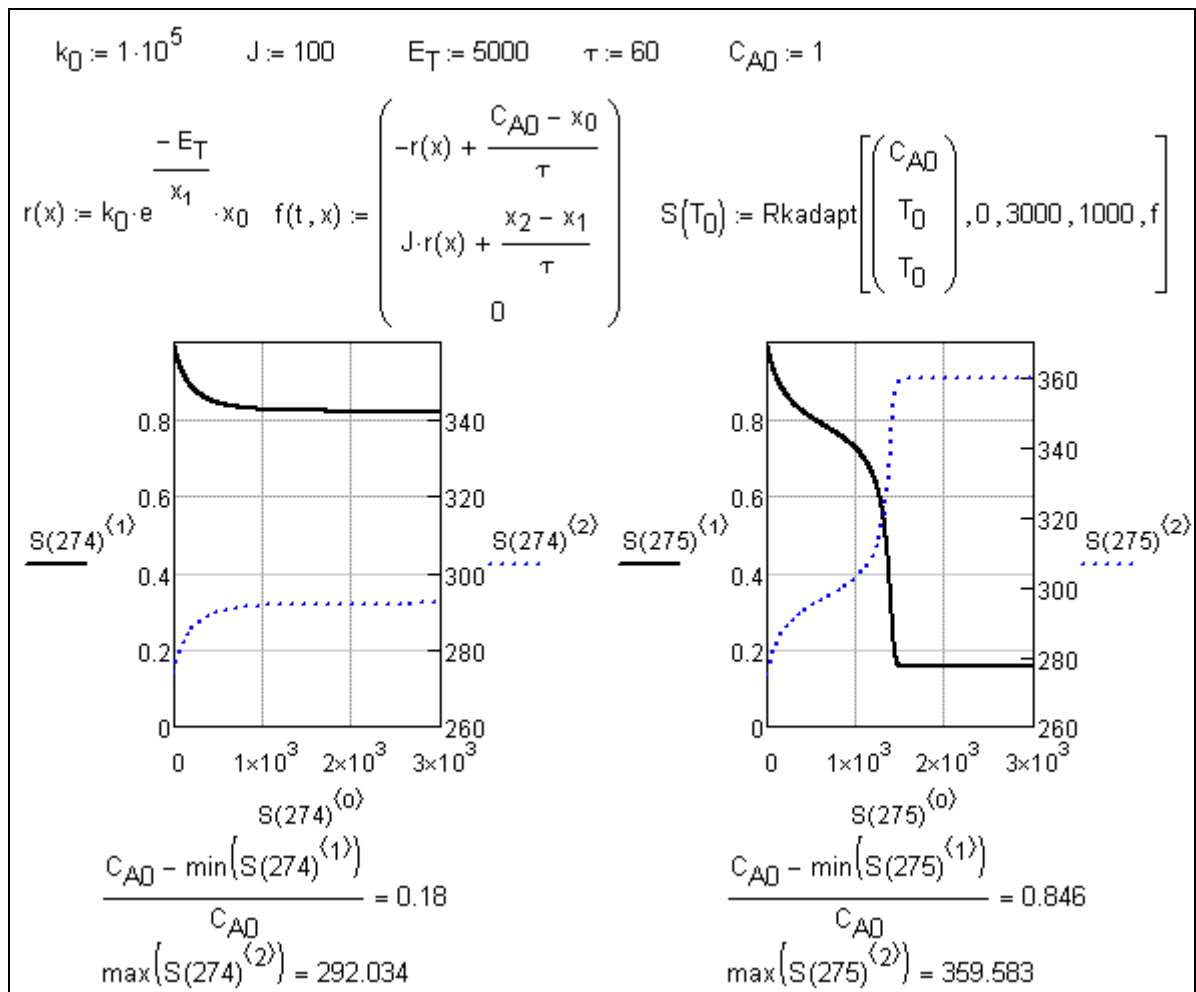


Fig. 3.28. Temperature and concentration trends in a flow adiabatic reactor

Thus, the processes taking place in technological reactors can have a **multistationarity** even for relatively simple kinetic schemes (in this case we consider a simple non-reversible first-order reaction). In practice, reactors work usually in the conditions close to stationary. Therefore, a problem of optimal organization of the reaction conditions becomes of great importance. In the discussed example the first stationary state is undesirable from the efficiency point of view.

For example, assuming $A=1 \cdot 10^5 \text{ s}^{-1}$, $E_d/R=5000 \text{ K}$, $J=100 \text{ K} \cdot \text{m}^3/\text{kmol}$, $\tau=60 \text{ s}$, initial concentration $C_{A0} = 1 \text{ kmol/m}^3$, and initial temperature $T_0 = 270 \text{ K}$, we can find three stationary states. Their quantitative properties are determined by the solutions of an algebraic equation set, to which the differential equation set is transformed when both $dC_A \llbracket dt$ and $dT \llbracket dt$ equal zero:

$$\frac{C_{A0} - C_A}{\tau} - A e^{-\frac{E_T}{T}} C_A = 0,$$

$$\frac{T_0 - T}{\tau} + J A e^{-\frac{E_T}{T}} C_A = 0.$$

$$\begin{array}{l}
 C_{A0} := 1 \quad \tau := 60 \quad A := 1 \cdot 10^5 \quad E_T := 5000 \quad T_0 := 270 \quad J := 100 \\
 \\
 \text{GIVEN} \quad \frac{C_{A0} - C_A}{\tau} - A \cdot e^{-\frac{E_T}{T}} C_A = 0 \quad \frac{T_0 - T}{\tau} + J \cdot A \cdot \exp\left(\frac{-E_T}{T}\right) \cdot C_A = 0 \\
 \\
 S(T, C_A) := \text{FIND}(T, C_A) \\
 \\
 \begin{pmatrix} T_{1st} \\ C_{1st} \end{pmatrix} := S(279, 0.9) \quad \begin{pmatrix} T_{2st} \\ C_{2st} \end{pmatrix} := S(322, 0.5) \quad \begin{pmatrix} T_{3st} \\ C_{3st} \end{pmatrix} := S(346, 0.2) \\
 \\
 \begin{pmatrix} T_{1st} \\ C_{1st} \end{pmatrix} = \begin{pmatrix} 278.996 \\ 0.91 \end{pmatrix} \quad \begin{pmatrix} T_{2st} \\ C_{2st} \end{pmatrix} = \begin{pmatrix} 322.089 \\ 0.479 \end{pmatrix} \quad \begin{pmatrix} T_{3st} \\ C_{3st} \end{pmatrix} = \begin{pmatrix} 346.28 \\ 0.237 \end{pmatrix} \\
 \\
 \text{Jacobian}(T, C_A) := \begin{pmatrix} \frac{1}{\tau} - A \cdot e^{-\frac{E_T}{T}} & -\frac{E_T}{T} \\ A \cdot J \cdot e^{-\frac{E_T}{T}} & \frac{A \cdot C_A \cdot E_T \cdot e^{-\frac{E_T}{T}}}{T^2} - \frac{1}{\tau} \end{pmatrix} \\
 \\
 \text{eigenvals}(\text{Jacobian}(T_{1st}, C_{1st})) = \begin{pmatrix} -0.017 \\ -8.683 \times 10^{-3} \end{pmatrix} \\
 \\
 \text{eigenvals}(\text{Jacobian}(T_{2st}, C_{2st})) = \begin{pmatrix} -0.017 \\ 7.055 \times 10^{-3} \end{pmatrix} \\
 \\
 \text{eigenvals}(\text{Jacobian}(T_{3st}, C_{3st})) = \begin{pmatrix} -0.017 \\ -0.017 \end{pmatrix}
 \end{array}$$

Fig. 3.29. Computations of possible stationary states and analysis of their stability

The presence of multistationarity can be illustrated in other way. The last two equations allow one to conclude that

$$\frac{T - T_0}{\tau} = JAe^{-\frac{E_T}{T}} \left(C_{A0} - \frac{1}{J} \left(T - T_0 \right) \right)$$

A left part of the obtained correlation depends linearly on the temperature T . Its value is proportional to the cooling rate caused by a hot ($T > T_0$) airflow out of the reactor. A right part corresponds to the heat generation rate in the reactor due to the reaction exothermicity. It is a non-linear function of temperature. If one plots the temperature dependences of the equation right and left parts, one will see their interception in points corresponding to the calculated stationary temperatures and concentrations (fig. 3.30).

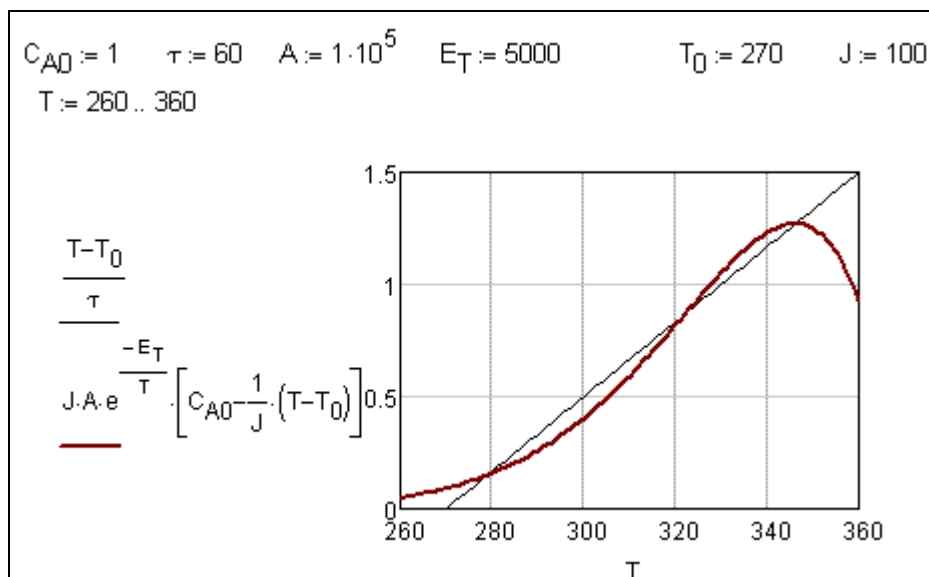


Fig. 3.30. Graphical representation of possible stationary states

When considering systems with many stationary states, it is important to investigate the stability of the latter. Stability of a stationary state is directly connected to the thermal stability of the reactor. It may happen that a small perturbation of the system takes it out of the unstable state. The process will convert into the other one, now stable. In this case calculations (fig. 3.29) show that two out of three possible stationary states are stable: for them the Jacobian matrix eigenvalues are real and of the same sign (stable node). The third stationary state has real, but negative, Jacobian eigenvalues (saddle point). A comparison of these results with the plots shown in fig. 3.30 allows one to conclude: a stationary state is stable if a slope of the heat elimination curve is smaller than a slope of the heat liberation.

Finally, we can prove the conclusions by plotting a phase portrait of the system (fig. 3.31). Here dots correspond to the possible stationary states. The phase paths for different initial temperatures are marked with bold lines.

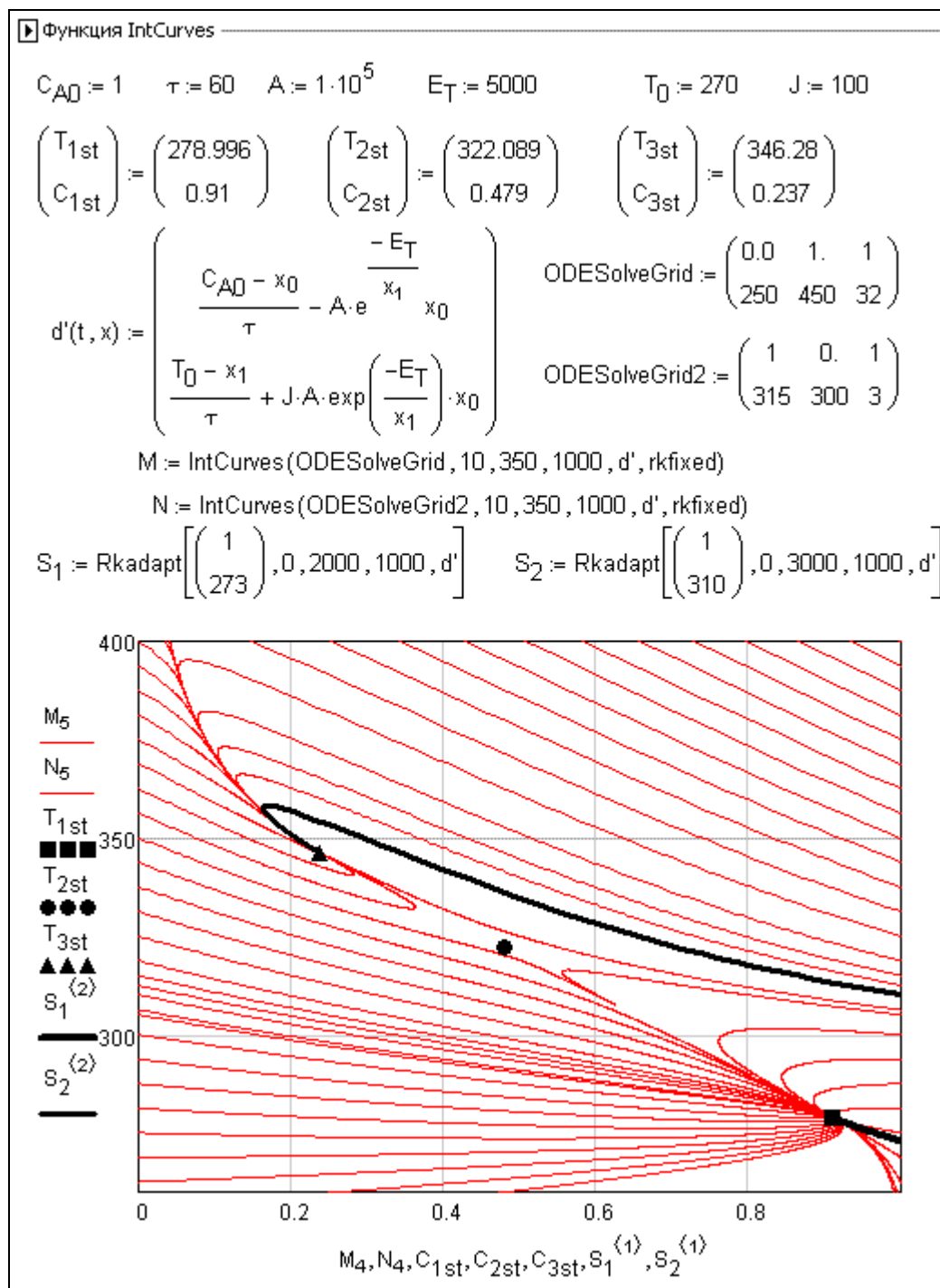


Fig. 3.31. Phase portrait for exothermic reaction in an adiabatic flow reactor

Fig. 3.31 allows us to see that one or another stationary state is realized according to the initial conditions.

The discussed examples by no means cover all possible problems of chemical kinetics as well as other differential models for chemical-engineering processes, on which the reactor theory is based.