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INTEGRATED ENVIRONMENT FOR SIMULATION OF CHEMICAL REACTION KINETICS

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This article briefly describes an integrated environment suitable for simulation of the kinetics of the chemical reactions. The term "simulation model" is presented in the article together with the well-known terms such as "reaction schema" and "mathematical model". The simulation model is suitable for solving the problems of reaction kinetics. Integrated environment can be used for simulation of biological processes and activated-sludge basins for the biological waste-water treatment.

Introduction

The former procedure of chemical reaction simulation was very elaborate and cumbersome. The main problems were in the area of determining the reaction constants, processing and storing of experimental values.

The solving of the differential equations system with initial conditions in terms of concentration vs. time was almost impossible and the programming of

suitable numerical method for each chemical reaction was a very lenghthy work. If the selected reaction schema did not match the measured values of concentration in time, it was necessary to try another reaction schema with a new system of differential equations and a new program.

The integrated environment removes all these problems and enables the transformation of mathematical model (the system of differential equations with initial conditions) into simulation model by the means of editor. The integrated environment allows work with this model. We can distinguish these three steps in the development of:

1) Reaction schema
2) Mathematical model
3) Simulation model

We present an example of simulation model development. The compounds M, K, C, D, P take part in a reaction with reaction constants k_1, k_2, k_3. (The experiment is described in Ref.[1]).

1) Reaction schema

$$D + P \xrightarrow{k_1} K$$

$$D + P \xrightarrow{k_2} C$$

$$K + D \xrightarrow{k_3} M$$

2) Mathematical model

$$\frac{d[M]}{dt} = k_3[K].[D]$$

$$\frac{d[K]}{dt} = k_1[D].[P] - k_3[K].[D]$$

$$\frac{d[C]}{dt} = k_2[D].[P]$$

$$\frac{d[D]}{dt} = -k_2[D].[P] - k_1[P].[D] - k_3[K].[D]$$

$$\frac{d[P]}{dt} = -k_1[D].[P] - k_2[D].[P]$$

Constants	$dm^3\ mol^{-1}\ min^{-1}$
k_1	3332.4
k_2	673.2
k_3	94.8

3) Simulation model

1st block: INTEGRATOR#1
Input: const#3*int#2*int#4
Initial value: 0

2nd block: INTEGRATOR#2
Input: const#1*int#4*int#5-const#3*int#2*int#4
Initial value: 0

3rd block: INTEGRATOR#3
Input: const#2*int#4*int#5
Initial value: 0

4th block: INTEGRATOR#4
Input: -const#2*int#4*int#5-const#1*int#5*int#4
-const#3*int#2*int#4
Initial value: 0.0000258

5th block: INTEGRATOR#5
Input: -(const#1+const#2)*int#4*int#5
Initial value: 0.0000258

6th block: UNIVERSAL#1
Input: 3332.4

7th block: UNIVERSAL#2
Input: 673.2

8th block: UNIVERSAL#3
Input: 94.8

Creation of the Simulation Model

The integrated environment is controlled by main menu with submenus with instructions for user.

MAIN MENU OF INTEGRATED ENVIRONMENT FOR SIMULATION OF CHEMICAL REACTION KINETICS		
* CHEMI *		* CHEMI *
* CHEMI *		* CHEMI *
MENU:		
Model name		
Edit model	Conditions	Simulation
Print model	Read table	
Reaction constants		
1. Save model	2. Load model	
3. Save conditions	4. Load conditions	
New model	Exit	
About ...		
Press the key of your selection!		

There are three constants k_1, k_2, k_3 named const#1, const#2, const#3 (or con#1, con#2, con#3). The searched concentrations [M], [K], [C], [D], [P] are named INT#1, INT#2, INT#3, INT#4, INT#5. The equations of the mathematical model are solved simultaneously in blocks INTEGRATOR#1 ... INTEGRATOR#5. We use identificators con#1, con#2, con#3 in such a case when we do not know the constants of the reactions and when we search their values. If we know the values of reaction constants and search the concentrations in time intervals, then we write to blocks UNIVERSAL#1, UNIVERSAL#2, UNIVERSAL#3. We write identificators uni#1, uni#2, uni#3 instead of const#1, const#2, const#3 as well.

The creation of simulation model and its editing are performed by the model editor. This editor is called by E key on keyboard (see the main menu). The model must be labelled by name (button J). The model is stored on disk under its name with .MOD extension (by pressing the button 1). The saved model can be loaded back into the system by pressing the button 2.

The creation of simple simulation model with its storing on disk takes no more than 5 minutes. The equations can be linear or nonlinear and can include mathematical functions as sin, cos, sqrt, exp, log, arctan, and abs.

The Table of Measured Values

It is necessary to compare the simulation results with measured values of concentrations in chemical reaction. The entering of measured values for this purpose is possible after pressing key N.

MEASURED VALUES *** dlask1ko ***	
Submitted times	Instructions:
	F2 = load table
	F3 = number of columns
1.	PgDn, PgUp = next/previuos time
	^, v = previous/next concentration
	←, →, Ins, Del, BackSp, Home, End, ^Home, ^End = Editation
	F9/F10 = delete/insert time
	F1 = main menu
	F4 = new table
	F5 = print
	F6 = save table

In the first column are values of time. The maximum of 10 concentration values is allowed. The number of concentration values can be set by pressing key F3. The table of measured values is labelled by name (key F6). The suffix .TAB is automatically added to this name. The table can be loaded back into system (key F2).

Conditions for Simulation

Condition for simulation can be set in menu "Conditions" (by key P). In this submenu it is possible to set the start and end time of simulation, step of simulation (for numerical integration methods), step of output listing, selection of integration method (highlighted digits 2, 4), printer output of results (highlighted letters N, A), output on screen is standard, and print of difference of computed and measured values (highlighted letter O, E).

CONDITIONS FOR SIMULATION *** dlask1ko ***	
Instructions	F1 = main menu
	PgDn, PgUp = next/previous window
	^, v = move cursor in window
	←, →, Ins, Del, BackSp, Home, End, ^Home, ^End = Editation
	F9 = cancel block
	Integration by the method Runge-Kutta: -- 2nd order, 4th order
Start of simulation: 0.000	Output of results to printer - No
End of simulation: 500	- Yes
Step of simulation: 0.1	Print the difference compared with experimental values - Yes
Step of printing: 50	- No

Simulation displays outputs of these blocks:

1st followed block: INTEGRATOR#1

2nd followed block: INTEGRATOR#2

3rd followed block: INTEGRATOR#3

4th followed block: INTEGRATOR#4

5th followed block: INTEGRATOR#5

6th followed block:

In the case we require to display the difference of simulation output values and experimental values (highlighted letter O), the conditions for simulation are extended as shown below.

CONDITIONS FOR SIMULATION *** dlask1ko ***	
Instructions	F1 = main menu
	PgDn, PgUp = next/previous window
	^, v = move cursor in window
	←, →, Ins, Del, BackSp, Home, End, ^Home, ^End = Editation
	F9 = cancel block
	Integration by the method Runge-Kutta: -- 2nd order, 4th order
Start of simulation: 0.000	Output of results to printer - No
End of simulation: 500	- Yes
Step of simulation: 0.1	Print the difference compared with experimental values - Yes
Step of printing: 50	- No

Simulation displays outputs of these blocks:	
1st followed block: INTEGRATOR#1	1st followed value: 1
2nd followed block: INTEGRATOR#2	2nd followed value:
3rd followed block: INTEGRATOR#3	3rd followed value:
4th followed block: INTEGRATOR#4	4th followed value:
5th followed block: INTEGRATOR#5	5th followed value:
6th followed block:	6th followed value:

In this expanded menu it is possible to set which computed concentrations of compounds will be displayed. In the right column it is possible to set an arbitrary column (1-10) in the measured values table. The difference is computed from the values on the same row.

Simulation

The simulation (key S) is a numerical solution of the simulation model. The conditions for simulation determine the process of simulation. The result of simulation is a table of concentration vs. time. The output can be viewed also as a graph - see Fig.1.

SIMULATION: *** dlask1ko ***

Start of simulation:	0.000
End of simulation:	500.000
Step of simulation:	0.100
Step of printing:	50.000

Simulation by the method Runge-Kutta of the 2nd order:

T	INT#1	INT#2	INT#3	INT#4	INT#5
0.000	0.00e+00	0.00e+00	0.00e+00	2.58e-05	2.58e-05
50.000	4.75e-07	1.74e-05	3.61e-06	3.87e-06	4.34e-06
100.000	7.03e-07	1.86e-05	3.91e-06	1.85e-06	2.55e-06
150.000	8.30e-07	1.90e-05	4.01e-06	1.09e-06	1.92e-06
200.000	9.09e-07	1.92e-05	4.07e-06	7.01e-07	1.61e-06
250.000	9.62e-07	1.93e-05	4.10e-06	4.72e-07	1.43e-06
300.000	9.98e-07	1.94e-05	4.11e-06	3.27e-07	1.33e-06
350.000	1.02e-06	1.94e-05	4.13e-06	2.31e-07	1.25e-06
400.000	1.04e-06	1.94e-05	4.13e-06	1.64e-07	1.21e-06
450.000	1.05e-06	1.94e-05	4.14e-06	1.18e-07	1.17e-06
500.000	1.06e-06	1.94e-05	4.14e-06	8.54e-08	1.15e-06

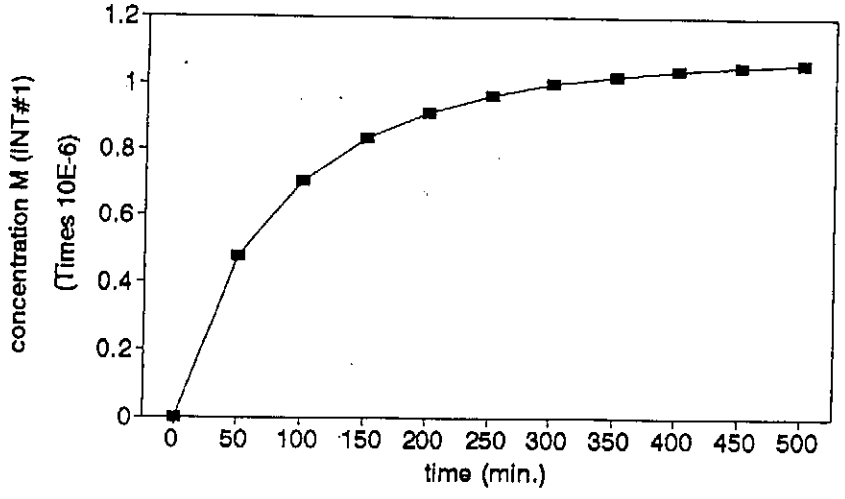

Fig. 1 The course of M vs. time

Computation of Reaction Constants

If the simulation model has reaction constants in the form of identificators const#1, const#2, const#3, it is possible to start the calculation of reaction constants (key R). The submenu of reaction constants has 4 windows. We can switch between them by keys PgDn, PgUp.

Window 1. reaction constants

COMPUTING OF REACTION CONSTANTS: *** dlask1ko ***		
1. reaction constants		
CONST#1: LL: 3000	UL: 3500	Instructions:
CONST#2: LL: 600	UL: 700	PgDn, PgUp = switch window
CONST#3: LL: 80	UL: 100	
		←, →, Ins, Del, BackSp, Home, End, ^Home, ^End = Editation
		F1 = main menu
		F5 = print
		f6 = computing of reaction constants
		Windows:
		1. Reaction constants
		2. Conditions of computing
		3. Monitoring of values
		4. Result of computing

In this window we set limits of expected values.
LL means lower limit
UL - " - upper limit

Window 2. conditions of computing

COMPUTING OF REACTION CONSTANTS: *** dlask1ko ***

2. Conditions for computing reaction constants:
permitted deviation of difference: 1.00e-03

Interval of time matching

from : 50 to: 500

Instructions:

PgDn, PgUp = switch window

←, →, Ins, Del, BackSp, Home, End, ^Home, ^End = Editation

F1 = main menu

F5 = print

F6 = computing of reaction constants

Windows:

1. Reaction constants
2. Conditions of computing
3. Monitoring of values
4. Result of computing

Here we set the permitted mean deviation of differences: experimental value - (minus) computed value, which is computed in time interval: from - to.
The permitted deviation is the average of percentual differences from measured values.

For example: 0.01 = 1%
0.1 = 10%

Window 3. monitoring of values

COMPUTING OF REACTION CONSTANTS *** dlask1o ***

3. The following blocks and columns are considered in computing:

1st foll. block:	INTEGRATOR#1	1st foll. value:	1
2nd foll. block:	INTEGRATOR#2	2nd foll. value:	
3rd foll. block:	INTEGRATOR#3	3rd foll. value:	
4th foll. block:	INTEGRATOR#4	4th foll. value:	
5th foll. block:	INTEGRATOR#5	5th foll. value:	
6th foll. block:		6th foll. value:	
7th foll. block:		7th foll. value:	
8th foll. block:		8th foll. value:	
9th foll. block:		9th foll. value:	
10th foll. block:		10th foll. value:	

Instructions:

PgDn, PgUp = switch window

←, →, Ins, Del, BackSp, Home, End,

^Home, ^End = Editation

F9 = erase row

F1 = main menu

F5 = print

F6 = computing of reaction constants

Windows:

1. Reaction constants
2. Conditions of computing
3. Monitoring of values
4. Results of computing

It is possible to choose the computed values in the left column and the measured ones in right column. Mean deviation is estimated from the differences, which is the origin of reaction constants computing. The mean deviation can be computed not only from differences of one reaction compound concentration, but also from several ones (maximally from 10).

Window 4, computed reaction constants

COMPUTING OF REACTION CONSTANTS: *** dlask1o ***	
4. Computed reaction constants:	
CONST#1:	Instructions:
CONST#2:	PgDn, PgUp = switch window
CONST#3:	F1 = main menu
	F5 = print
	F6 = computing of constants
	Windows:
	1. Reaction constants
	2. Conditions of computing
	3. Monitoring of values
	4. Results of computing

In this window the reaction constants are displayed. They were computed from the data in windows 1,2,3.

Conclusion

This integrated environment (2) is not complete yet. It will be extended in the estimating of initial concentrations so that the required concentration could be reached in a given time.

However, the present state of the integrated environment enables to simulate any reaction schema quickly and comfortably, to find out whether this reaction schema corresponds to the reaction (which is described by measured values of concentration), and to compute reaction constants. If we have the measured values in the file, the creation and simulation of one model takes about 5 minutes (without computing of reaction constants). The main menu and the submenus contain suggesting commentary. The maximum number of differential equations is 50, that of rate constants is 25. The program occupies 165 520 bytes. The step of integration could be chosen in menu "CONDITIONS FOR SIMULATION". The chosen step is constant during integration. No knowledge of programming is needed on the side of the users of systeme. This method seems to be an outstanding progress in comparison with others.

References

1. Plocek J., Dlask V.: Dyes and Pigments **26**, 307 (1994).
2. Kuechler J., Němcová A., Plocek J.: *Program for Simulation of Chemical Reaction Kinetics (program on disk)*, 1995.