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The Network Method for Solutions of Oscillating Reaction-Diffusion Systems

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The network approach is a method whereby physicochemical systems are replaced by electrical networks, which are simulated by using a digital computer program such as PSPICE. The network method solves problems of great mathematical complexity in a versatile and efficient way. This method has been applied to a system involving coupled chemical reactions and diffusion (Brusselator system) as a prototype of an oscillating reaction system. © 1995 Academic Press, Inc.

1. INTRODUCTION

In this paper we apply an alternative method to study dissipative nonlinear systems, such as systems involving coupled chemical reactions and diffusion, based on a network model of the diffusion-reaction equations. The technique derives from the theories of Peusner [1] and Oster *et al.* [2], known as network thermodynamics, which permit coupled flows and driving forces to be analyzed in terms of electrical networks. Network thermodynamics takes advantage of the similarities in the mathematical structure underlying different phenomena with balance and constitutive equations of the same type. Such equations fix the topology (the connection modes of the circuit branches) and the geometry (the circuit elements: resistors, capacitors, sources, etc.) of the network model, thus allowing us to establish a formal similitude between the diffusion-reaction equations and electric networks.

In the network approach, the spatial variable in the diffusion-reaction equations is discretized as in finite-difference schemes but the time variable remains continuous. This allows the mathematical model to be described by a network model, transforming the partial differential equations involved in the diffusion reaction problems into a set of coupled linear ordinary differential equations (equations of the network). When the network model of a system has been developed, an electrical network whose topology and geometry are identical with those of the system is obtained, and therefore the behavior of the network model is identical with that of the system. Highly developed methods of circuit analysis may then be employed to obtain the dynamic behavior of such systems directly from the graph without having to deal explicitly with the differential equations. We have found that the electric simulation program PSPICE [3] is very useful for this purpose. Although this program is designed as an electronic circuit simulator, it can be useful as a high-level user-oriented simulation language, specially suited to the digital solution of diffusion reaction problems.

Although reaction-diffusion systems have been studied with this approach, the study was done considering single chemical reactions [4] or very specific problems with special features, such as electroanalytical electrode processes [5] and sorption onto mineral surfaces [6]. In this paper, a logical extension of the previous work in the area of PSPICE simulation of reaction-diffusion network models is carried out with a relatively complex system of coupled reactions as the trimolecular model involving the following sequence of reactions under open-system conditions [7, 8]:

$$A \xrightarrow{k_1} X$$

$$2X + Y \xrightarrow{k_2} 3X$$

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$$B + X \xrightarrow{k_3} Y + D$$
$$X \xrightarrow{k_4} E. \qquad (1)$$

2. NETWORK MODELING OF DIFFUSION-REACTION PROCESSES

The one-dimensional diffusion-reaction process is described by the partial differential equation

$$\partial c(z, t)/\partial t = D\{\partial^2 c(z, t)/\partial z^2\} + f(c), \qquad (2)$$

where the diffusion coefficient, D, is assumed to be constant, $c(z, t)$ is the concentration of the chemical species at position z and time t, and the function, $f(c)$, represents a simultaneous chemical reaction.

The standard approach to solving Eq. (2) is to generate a system of finite difference equations. In the network approach, the space is the only discretized parameter, and Eq. (2) can be approximated as

$$dc_i/dt = (D/\Delta z^2)(c_{i-1} - 2c_i + c_{i+1}) + f(c_i), \qquad (3)$$

where the variable z has been partitioned into N discrete elements of width Δz. c_i is the concentration in the compartment i $(1 < i < N)$.

Equation (3) can be approximated as

$$dc_i/dt = (J_{i-1} - J_i)/\Delta z + f(c_i), \qquad (4)$$

where J_i is the flux leaving the compartment i

$$J_i = (D/\Delta z)(c_i - c_{i+1}) \qquad (5)$$

according to Fick's first law. However, Eq. (4) can be rewritten in the form

$$J_{i-1} - J_i - J_{c_i} + J_{G_i} = 0, \qquad (6)$$

where

$$J_{ci} = \Delta z\,(dc_i/dt) \qquad (7)$$

and

$$J_{Gi} = \Delta z f(c_i). \qquad (8)$$

Equations (5) and (7) in an electrical variable, Φ, correspond to the circuit equations for a resistor ($I = \Delta\Phi/\mathbf{R}$) and a capacitor $\{I = \mathbf{C}(d\Phi/dt)\}$, respectively. Thus, we can model J_i and J_{ci} as the current through a linear resistor of resistance $\mathbf{R} = \Delta z/D$ and as the current across a capacitor of capacitance equal to the thickness of the compartment, $\mathbf{C} = \Delta z$, respectively.

In the case of chemical reactions of order higher than the first, the function $f(\{c_i\})$ depends on the concentrations of all reaction species. Equation (8) is then a relation in which a "current," J_{Gi}, appears as a function of several "voltages" (the concentrations of the reaction species, $\{c_i\}$), which can be modeled by a multivariable voltage dependent current source ($\mathbf{GJ_G}$) of output $\Delta z \cdot f(\{c_i\})$. The network simulation is accomplished through a circuit simulation program such as PSPICE, and this program has a special format to write such nonlinear elements in a straightforward way [3].

On the other hand, Eq. (6) is Kirchhoff's current law at the node i, and we can incorporate both diffusive and reaction effects by connecting the three elements: a series resistance $\mathbf{R}$, a shunt capacitance $\mathbf{C}$, and a shunt dependent source $\mathbf{GJ_G}$ as in Fig. 1a. Since the diffusion coefficient is considered constant,

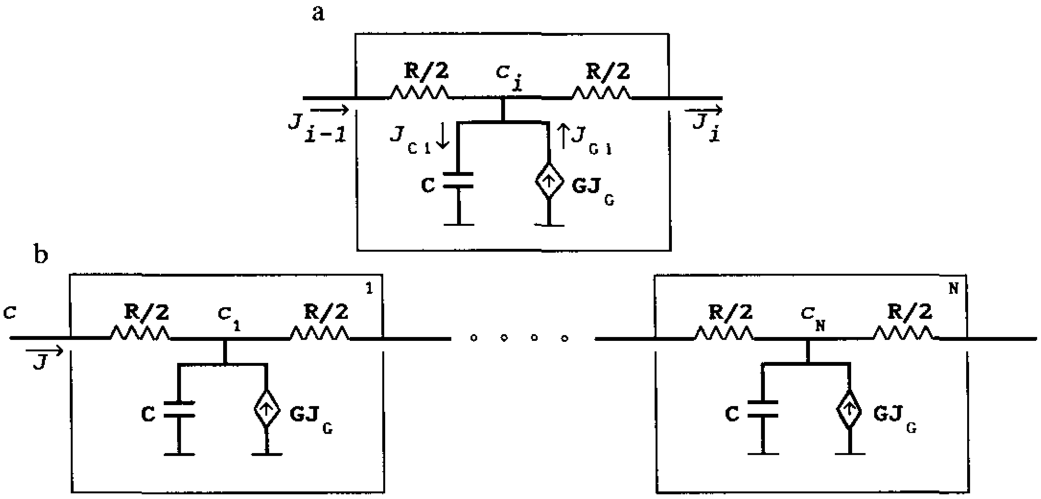

FIG. 1. Network model for a diffusion-reaction process: (a) in a compartment, (b) in the entire physical region.

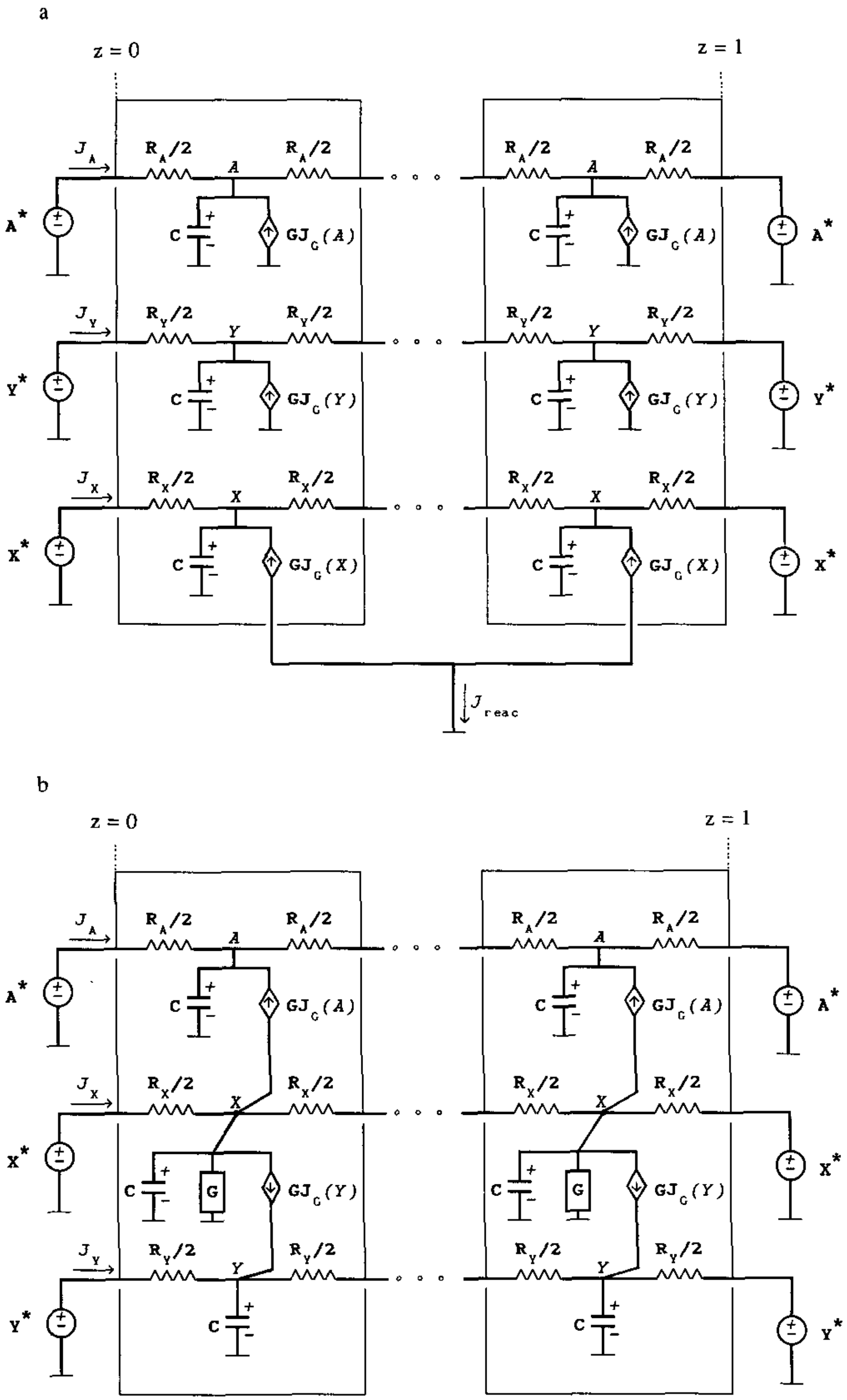

FIG. 2. (a) Network model for the Brusselator. (b) Another way to represent the global network model for the Brusselator.

TABLE I

Transient Analysis of Brusselator as in Fig. 2a; Accuracy and Computer Times

N	X (arbitrary units)	Y	CPU times on PC 486/66 (s)
60	36.65	2.10	140
100	19.78	3.89	284
120	19.16	4.00	353
140	17.66	4.35	434
160	16.86	4.55	491
200	16.54	4.64	650
240	16.54	4.64	1110

Note. Parameters used in the simulation (domain II) are: $D_A = 0.197$, $A^* = 14$, $D_X = 1.05 \times 10^{-3}$, $X^* = 14$, $D_Y = 0.66 \times 10^{-3}$, $Y^* = 5.5$, $B = 77$ (from Herschkowitz-Kaufman and Nicolis, 1972).

at least within each compartment, the linear resistor can be split into two equal parts, **R**/2, between which the capacitor and current source are placed. So, c_i in each compartment is the concentration in the center of such a compartment.

For network modeling purposes, any number, N, of circuit elements, like that in Fig. 1a, must be connected in series to form the network model for the entire physical region undergoing a non-stationary diffusion-reaction process. Figure 1b shows the entire ladder network model.

3. APPLICATION TO AN AUTOCATALYTIC MODEL

We apply this method to study an autocatalytic model of an open system adapted from the trimolecular model scheme (1) in the case where the concentrations of the substances B, D, and E are maintained space- and time-independent throughout the system [9]. The inverse reaction rates are neglected and all forward kinetic constants are set equal to one. The scheme is then described by the rate equations:

$$\partial X/\partial t = D_X(\partial^2 X/\partial z^2) + A + X^2Y - (B + 1)X \quad (9)$$

$$\partial Y/\partial t = D_Y(\partial^2 Y/\partial z^2) + BX - X^2Y \quad (10)$$

$$\partial A/\partial t = D_A(\partial^2 A/\partial z^2) - A \quad (11)$$

with $0 < z < l$.

We study the solutions of Eqs. (9)–(11) under the following boundary conditions:

$$X(0) = X(l) = X^* \quad (12)$$

$$Y(0) = Y(l) = Y^* \quad (13)$$

$$A(0) = A(l) = A^*. \quad (14)$$

Equations (9)–(11) take the form of the general diffusion-reaction problem (Eq. (2)), where the chemical kinetic terms, $f(\{c\})$, are now

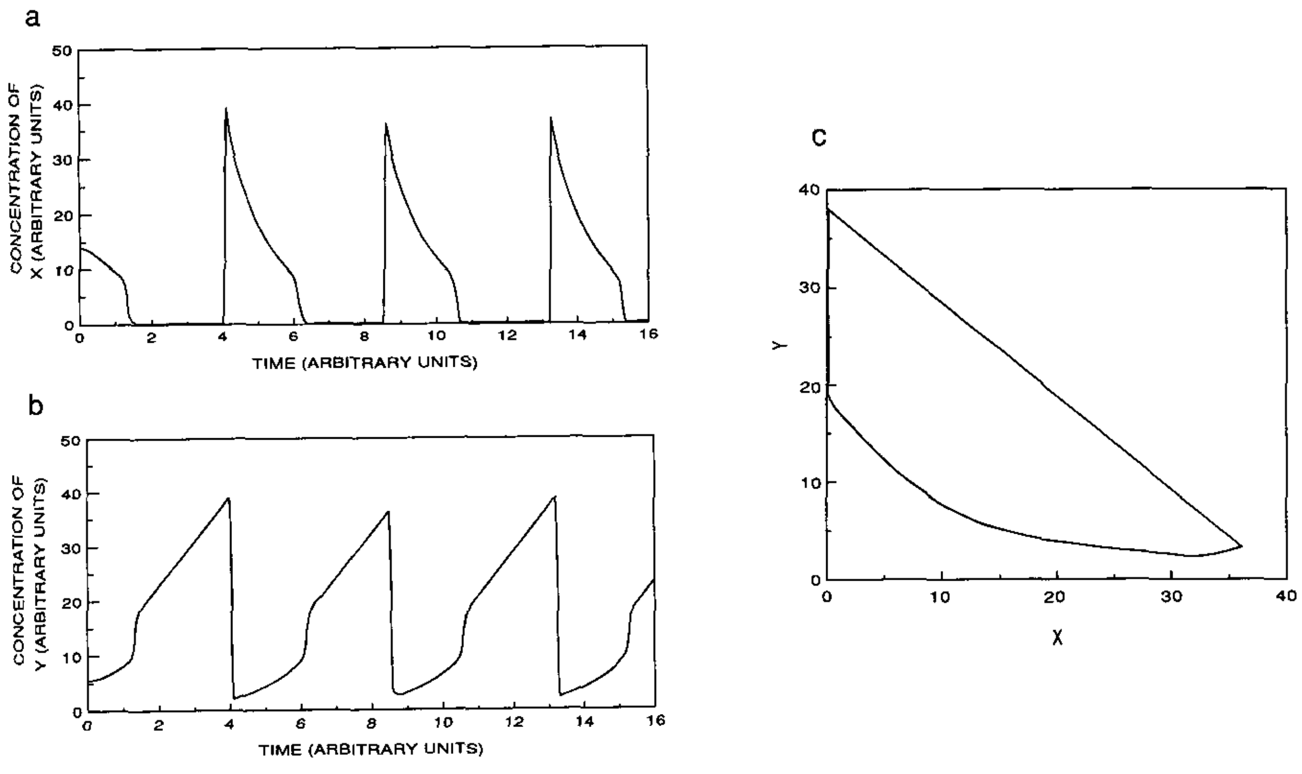

FIG. 3. Time evolution of the concentrations of X (a) and Y (b) at the middle point for domain II. (c) Plots of Y against X.

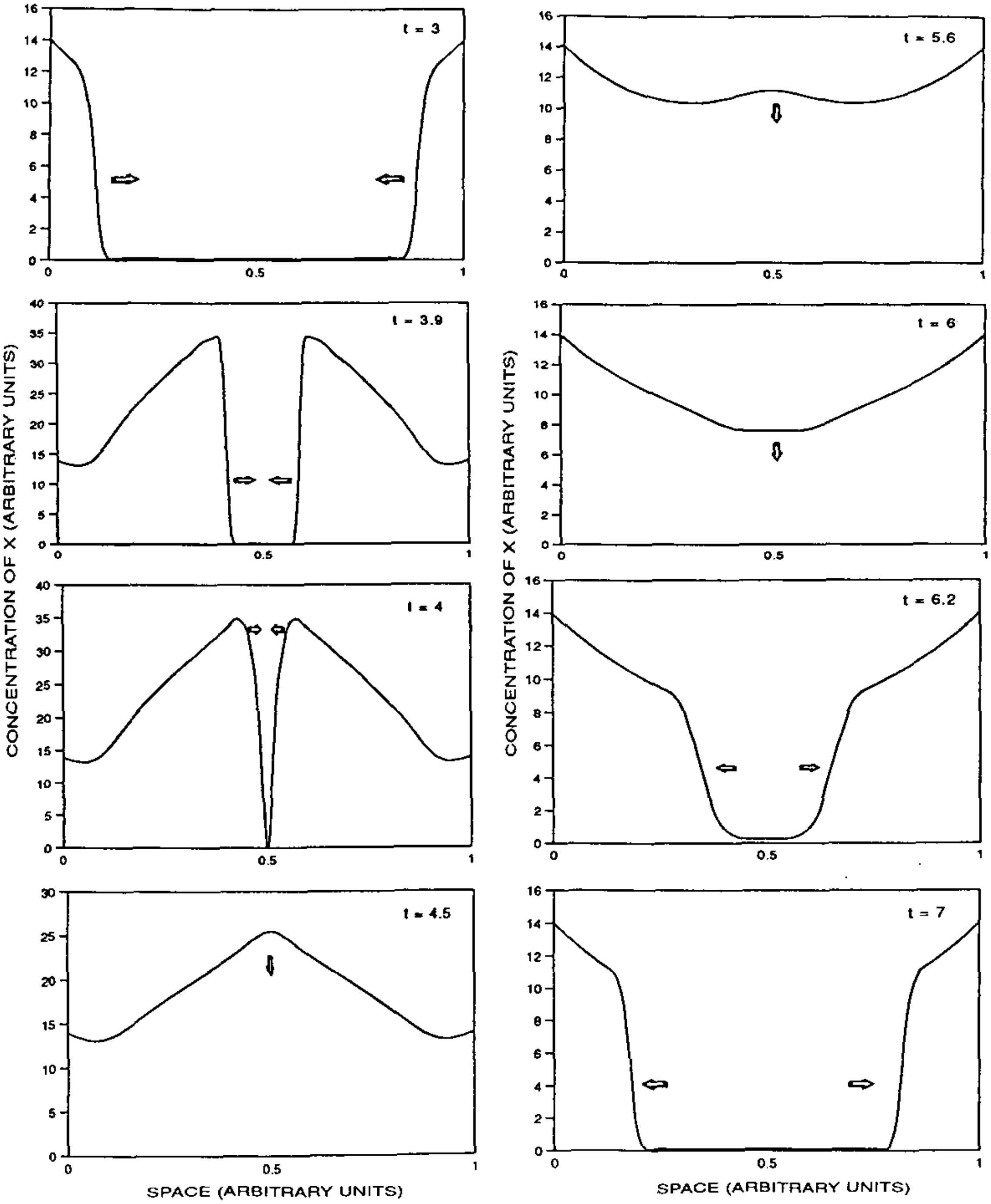

FIG. 4. Spatial distribution of X to certain characteristic stages of temporal evolution: t = 3, 3.9, 4, 4.5, 5.6, 6, 6.2, and 7. The numerical values of the various parameters are the same as in Table I.

$$f_X(\{c\}) = A + X^2Y - (B + 1)X \tag{15}$$

$$f_Y(\{c\}) = BX - X^2Y \tag{16}$$

$$f_A(\{c\}) = -A. \tag{17}$$

So, the network model of these equations will be the ladder network model of Fig. 1, with $\mathbf{GJ_G(X)} = \Delta z \cdot f_X(\{c\})$, $\mathbf{GJ_G(Y)} = \Delta z \cdot f_Y(\{c\})$, and $\mathbf{GJ_G(A)} = \Delta z \cdot f_A(\{c\})$ for the circuit branches representing the species X, Y, and A, respectively.

The next step is to include initial and boundary conditions in the network model. Equation (12)–(14) mean that the concentration of substances X, Y, and A maintain their initial values in $z = 0$ and $z = 1$. For network modeling purposes, these conditions can be represented by suitable constant voltage sources of values X^*, Y^*, and A^*, as shown for $z = 0$ and $z = 1$, in Fig. 2a. Moreover, any initial conditions can also be incorporated into the network model by means of the initial voltage of the capacitors of Fig. 2a, which shows the global network model for the Brusselator with above-mentioned conditions.

Since $\mathbf{GJ}_\mathrm{G}(\mathbf{X}) = -(\mathbf{GJ}_\mathrm{G}(\mathbf{A}) + \mathbf{GJ}_\mathrm{G}(\mathbf{Y}) + \Delta z\, X)$ we can improve the graphical representation of the dynamical behavior of the system connecting the A, X, and Y circuit branches as shown in Fig. 2b and where the term $\Delta z\, X$ has been modeled as the current through a linear conductance of value $\mathbf{G} = \Delta z$. Now, the network model of Fig. 2b represents graphically the interconnection among the flows J_A, J_X, and J_Y. In each point of the system, the terms of production (chemical reaction) and transport (diffusion) affecting the temporal variation of concentration of the species A, X, and Y have been made explicit graphically.

The implementation of the network model of Fig. 2 into an electric network simulation program, such as PSPICE, allows us to investigate the behaviour of the system for different situations. PSPICE is a member of the SPICE family of nonlinear circuit simulators which can calculate the behavior of analog circuits with speed and accuracy. PSPICE is a general purpose simulation program for nonlinear dc, ac, and transient analyses which can be run on a personal computer. A combination of trapezoidal (the implicit Crank–Nicolson scheme) and Gear's algorithm with a truncation-error timestep control is employed in the PSPICE program. This integration technique is stiffly stable.

PSPICE must be supplied with a netlist description of the circuit to be simulated and also with the set of analyses to be performed. This information is collected into an input file to be read by the simulator, which then calculates the "voltages" and "currents" of the analog components and nodes. The results are displayed as meaningful graphs and tables for further analysis.

The format for entering a description of the network into the program PSPICE is quite simple, and a complete explanation is given in the user's guide [3]. The actual PSPICE circuit file for a network model such as Fig. 2a, with the appropriate numerical values for the parameters of the system, is given in Appendix A for reference. All the calculations were carried out on a PC-486/66.

4. NUMERICAL RESULTS AND DISCUSSION

By means of the network model of Fig. 2, a quantitative simulation of the trimolecular model can be obtained by using the computer program PSPICE. Various parameters can be varied singly or in combination to explore their effect on model behavior. The result is the ability to perform a series of simulations in one computer run. Without attempting to present a complete catalogue of results for every choice of imput parameter, we will illustrate the versability and generality of the procedure by presenting some typical results for the above-mentioned autocatalytic system. The results obtained are consistent with those of other authors [8, 9], despite the use of different methods.

Using the network thermodynamic method, we showed in a previous paper [10] that, in the limit where A is distributed uniformly in the system ($D_A \to \infty$), the scheme (1) presents a unique uniform steady state solution,

$$X_0 = A, \qquad Y_0 = B/A, \tag{18}$$

which is the continuation of the close-to-equilibrium behavior. For certain sets of values of the system parameters, A, B, D_x, and D_y, the solution of (18) became unstable. Herschokowitz-Kaufman and Nicolis [9] have carried out an infinitesimal stability analysis of system (Eqs. (9)–(11)) to analyze the possible existence of additional steady-state solutions of the dissipative structure type. Their results show that, for fixed values of A, D_x, and D_y, the domain of instability may be divided into two regions: one with B small and D_y much larger than D_x (domain I), and another with B large and D_y close to, or smaller, than D_x (domain II).

In the first place, we have carried out a transient analysis of the network model, for values of B and D_y belonging to the unstable domain II. The accuracy of the network simulation goes up rapidly as the number of compartments (N) is increased. Therefore, we need to know the number of compartments needed to obtain reasonable numerical accuracy. In order to check out this effect, a multicompartment study has been carried out on the space $0 \leq z \leq l = 1$, taking compartments of thickness $\Delta z = 1/N$. Computed values of X and Y at middle point (point $N/2$) and at $t = 5$ for various numbers of compartments (N) have been listed in Table I. Beyond 140 compartments, the values of X and Y are not suffering very significant changes, while the cost in computer times increases with N; for that reason, in this paper a 140-compartment network model has been used.

The results of the network simulation for $N = 140$ and values of the system parameters belonging to unstable domains II and I are present in Figs. 3–7. Figure 3 shows the time variation of the concentrations of X and Y at the middle point and their phase diagram for domain II. Also, the spatial distribution of X to certain characteristic stages of temporal evolution, $t = 3$, 3.9, 4, 4.5, 5.6, 6, 6.2, and 7, is shown in Fig. 4. These times were chosen according to the results obtained for concentrations of X in Fig. 3a. So, we start at $t = 3$ with a minimum value of X at the middle point. After a time interval $\Delta t \cong 4.6$, the whole phenomenon is repeated and the system passes through exactly the same stages. These results imply that the system exhibits a "wavelike solution" with a sharp periodicity [9].

Figure 5 illustrates the concentration of X profiles at different times in the situation in which B is relatively smaller and D_y

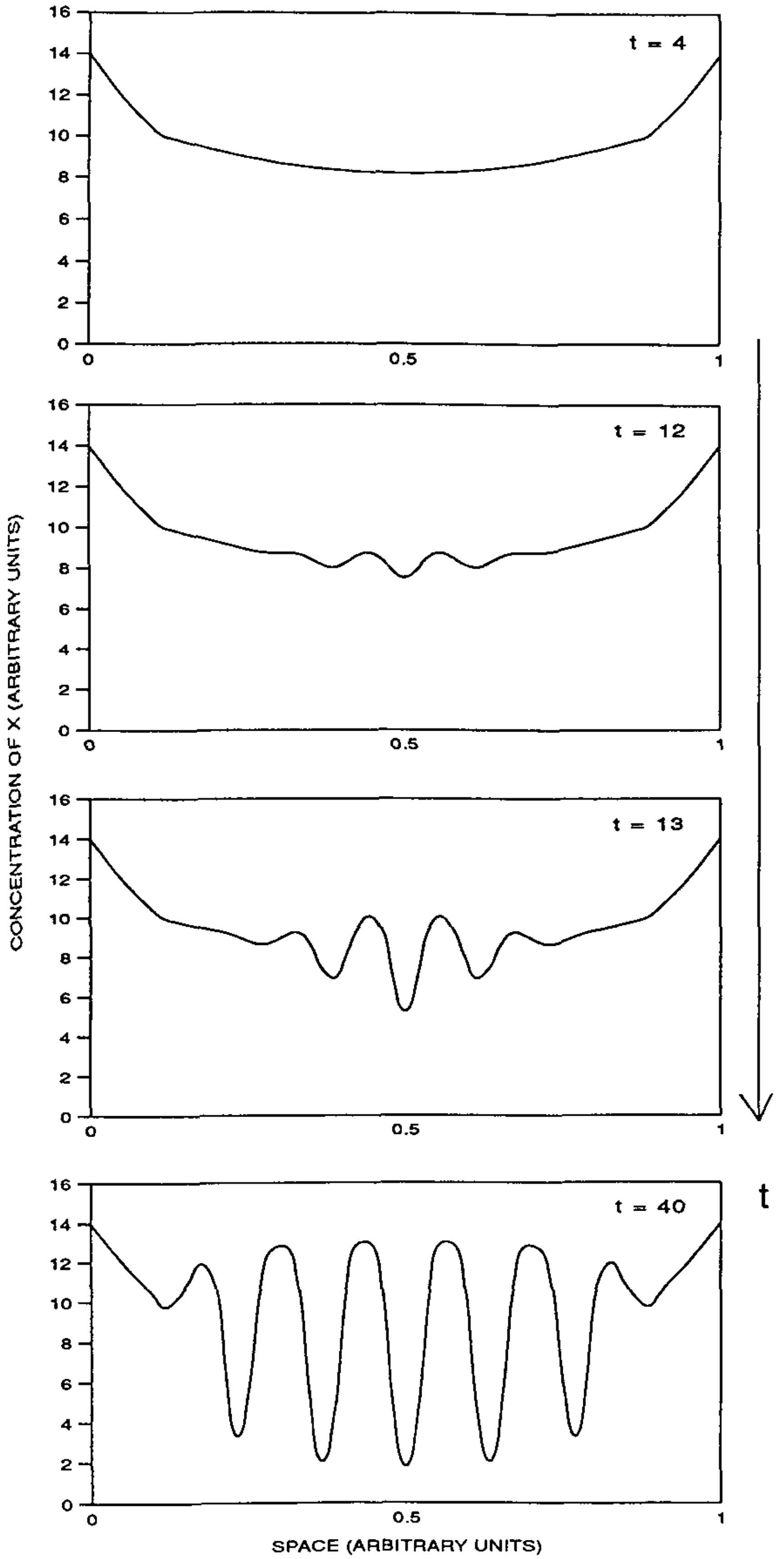

FIG. 5. Time evolution toward a new steady state characterized by a space organization of X. Parameters used in the simulation (domain I) are $D_A = 197 \times 10^{-3}$, $A^* = 14$, $D_X = 1.05 \times 10^{-3}$, $X^* = 14$, $D_Y = 5.25 \times 10^{-3}$, $Y^* = 1.86$, and $B = 26.0$ (from Herschkowitz-Kaufman and Nicolis, 1972).

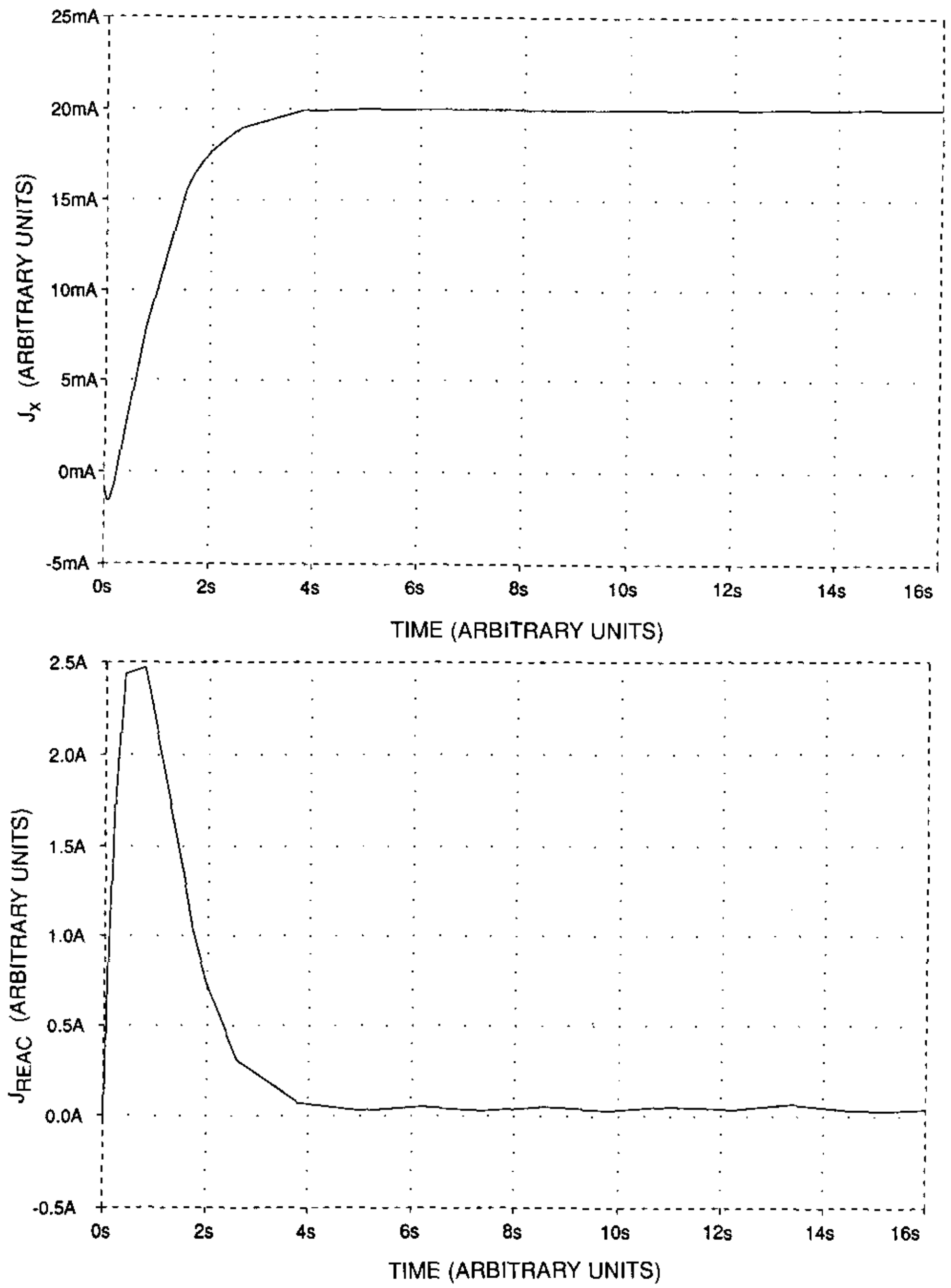

FIG. 6. Transient buildup of X total flux (J_X) and its rate reaction (J_{REAC}) for the domain I.

much larger than D_x (domain I). As can be seen from this figure, the system evolves toward a new steady state characterized by a space organization of X and Y (a localized dissipative structure).

Finally, to illustrate other possibilities that can be easily obtained from the network approach, Figs. 6 and 7 show the transient buildup of X total flux (J_x) and its rate reaction (J_{reac}) for domains I and II, respectively. The fluxes resulting show that for the first domain of instability the system finally attains a new steady state. However, in the second domain of instability the fluxes have an oscillating behavior in accordance with those observed in the time variation of X concentration at every point of the physical region of interest. So, in this case, the system evolves toward a steady state corresponding to a dissipative structure which is both space and time dependent.

5. CONCLUSION

The proposed network model together with an electric circuit simulation program such as PSPICE allows us to predict easily the behavior of the Brusselator. Both spatial and temporal distri-

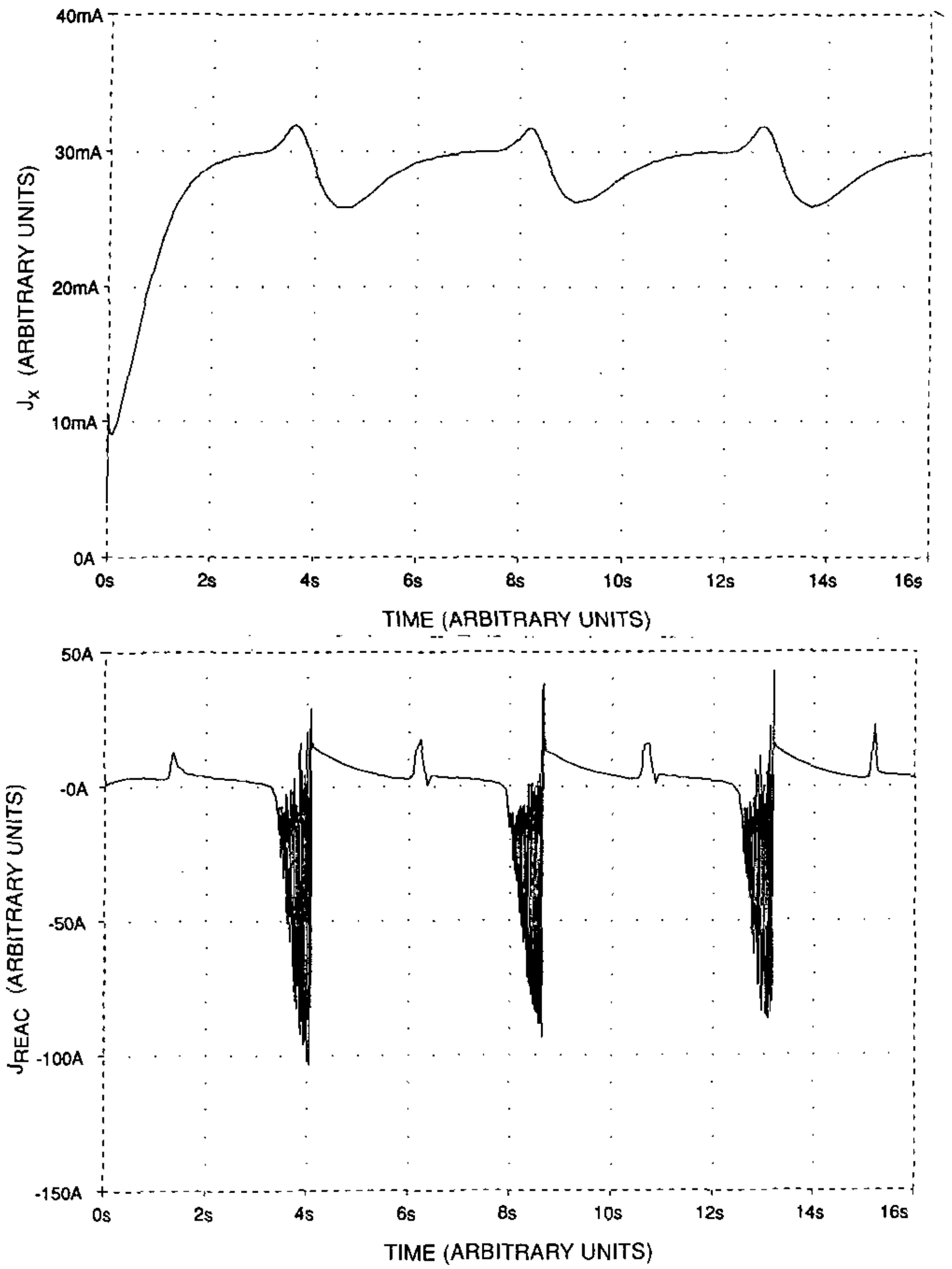

FIG. 7. Transient buildup of X total flux (J_X) and its rate reaction (J_{REAC}) for the domain II.

butions of species X and Y, as well as their fluxes, are obtained without mathematical complexities, providing a useful tool in the analysis of these kinds of systems where oscillatory phenomena arise, whatever the initial and boundary conditions.

The network method is simple because only a few branch elements are necessary and they are connected in such a way that Kirchhoff's laws of currents and voltages are fulfilled. When the network simulation using the electric simulation routine PSPICE is made, it is not necessary to extract or manipulate the equations which describe the network, because this program does that automatically. Therefore it is not necessary to consider either numerical or computational aspects. Moreover, this method is not limited by the complexity of the processes occurring in the system and allows one to solve complex mathematical problems by an efficient graphical method with a moderate cost in computer time.

One particular advantage of the method used here is that the investigator need not be familiar with computer programming and need only learn a few rules for providing information to PSPICE, which uses a simple and concise language to represent circuit diagrams. This is generally not the case when classical methods are used.

APPENDIX

PSPICE Program for the Network Model in Figure 2a

```
BRUSSELATOR
**** Values of the parameters: A = 14; X = 14; Y = B/A; N ≃ 140; Δr = 1/140
**** Domain I: DA = 197E-3; DX ≈ 1.05E-3; DY ≈ 5.25E-3; B = 26
**** Domain II: DA = 197E-3; DX =1.05E-3; DY ≈6.6E-4; B = 77
**** Subcircuit for the trimolecular scheme in a compartment (Domain I) ****
.SUBCKT TRIMOL 1 2 3 4 5 6 7
RY1 1 8 6.762E-1
RY2 8 2 6.762E-1
RX1 3 9 3.401
RX2 9 4 3.401
RA1 5 10 1.81E-2
RA2 10 6 1.81E-2
CY 8 0 7.1E-3 IC=1.86
CX 9 0 7.1E-3 IC=14
CA 10 0 7.1E-3 IC=14
GJG(A) 0 10 10 0 -7.1E-3
GJG(y) 11 8 POLY(2) 9 0 8 0 0 1.846E-1 0 0 0 0 0 -7.1E-3
GJG(X) 7 9 POLY(3) 9 0 8 0 10 0 0 -1.917E-1 0 7.1E-3 0 0 0 0 0 0 0 7.1E-3
.ENDS TRIMOL
**** Network Simulation for N = 140 ****
X1 2000 2001 3000 3001 4000 4001 1 TRIMOL
X2 2001 2002 3001 3002 4001 4002 1 TRIMOL
X3 2002 2003 3002 3003 4002 4003 1 TRIMOL
X4 2003 2004 3003 3004 4003 4004 1 TRIMOL
              .
              .
              .
              .
X138 2137 2138 3137 3138 4137 4138 1 TRIMOL
X139 2138 2139 3138 3139 4138 4139 1 TRIMOL
X140 2139 2140 3139 3140 4139 4140 1 TRIMOL
**** Boundary conditions, r = 0 ****
VY 2000 0 1.86
VA 4000 0 14
VX 2 0 14
**** X total flux and rare reaction of X ****
VJx 2 3000 0
VJreac 1 0 0
**** Boundary conditions, r = 1 ****
VY2 2140 0 1.86
VX4 3140 0 14
VA6 4140 0 14
**** Transient analysis ***
.TRAN 1 16 UIC
.PRINT TRAN V(2000) V(2001) .... V(2139) V(2140)
.PRINT TRAN V(3000) V(3001) .... V(3139) V(3140)
.PRINT TRAN V(4000) V(4001) .... V(4139) V(4140)
.PRINT TRAN I(VJx) I(VJreac)
.PROBE
.END
```

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