Simulation of First-Order Chemical Kinetics Using Cellular Automata

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Cellular automata are dynamical systems composed of arrays of cells that change their states in a discrete manner following local, but globally applied, rules. It is shown that a two-dimensional asynchronous cellular automaton simulates both the deterministic and the stochastic features of first-order chemical kinetic processes in an especially simple manner, avoiding the chore of solving either the deterministic coupled differential rate equations or the stochastic master equation. Processes illustrated include first-order decay, opposing first-order reactions, consecutive reactions, the steady-state approximation, a rate-limiting step, pre-equilibrium, and parallel competing reactions. The deterministic solutions are seen to emerge as statistical averages in the limit of large cell numbers. Some additional stochastic and statistical features of the solutions are examined.

INTRODUCTION

In the usual macroscopic *deterministic* approach to chemical kinetics, coupled differential equations (rate equations) are solved, sometimes analytically, but often by numerical methods because of their complicated forms. The evolution of a system is considered to be continuous and completely determined by the rate equations. Despite its widespread use and undeniable utility, it has been noted that the deterministic approach lacks sound theoretical justification, and its employment is based on empiricism.[1] Stochastic analysis provides an alternative approach based upon the fundamental probabilistic and discontinuous microscopic events that underlie macroscopic changes.[2] Under reasonable assumptions these latter events are seen to represent random Markov processes.[1,3] Gillespie[4−6] has shown that a stochastic approach, based on Monte Carlo procedures and realized by computer simulation, correctly describes the stochastic aspects of the solutions that are necessarily ignored in the deterministic approach. Nonetheless, the mathematical structure of the stochastic approach can be daunting and the stochastic master equation itself is frequently "mathematically intractable".[4]

The purpose of this report is to show that *cellular automata* provide a direct and attractive means for simulating the stochastic approach. In particular, it will be shown that the salient features of first-order chemical kinetics, both deterministic and stochastic, can be accurately simulated within this framework without the necessity of solving the coupled rate equations. Certain statistical aspects of the cellular automaton system will also be investigated. In later reports we shall demonstrate that cellular automata also effectively simulate second-order rate processes, enzyme kinetics, and other phenomena.

CELLULAR AUTOMATA

Cellular automata (CA) were first introduced by Ulam[7,8] and von Neumann[9] nearly 50 years ago. They have been defined in a number of ways, of which the following is typical:[10]

> [Cellular automata] are one-, two-, or three-dimensional lattices built out of cells. Each cell can be at any given time in one of several possible states. The transitions between states from one time-step to the next depend on the states of the cell and its neighbors. They are determined by well-specified rules, the same rules for all cells and all time. A kind of *microcausality* governs the evolution of such automata.

Several authors have noted that although differential equations are currently used for most models of natural systems, cellular automata provide an attractive, and in some ways complementary, alternative.[11−13]

A cellular automaton is therefore a dynamical system that evolves in accord with certain local rules. Wolfram has given five basic defining characteristics of cellular automata:[11] (1) They consist of a discrete lattice of sites. (2) They evolve in discrete time-steps. (3) Each site takes on a finite set of possible values. (4) The value of each site evolves according to the same deterministic rules. (5) The rules of the evolution of a site depend only on a local neighborhood of sites around it. The discrete nature of cellular automata makes them ideally suited for implementation on digital computers.[14] Moreover, although the operational rules for the automata are often quite simple, surprisingly complex and informative behaviors can result from their implementation. Indeed, it is just these complex behaviors, sometimes referred to as *emergent properties*, that are often the principal interest of a cellular automata study. A recent review on cellular automata can be consulted for further descriptions.[14]

CA models have been applied to a wide variety of phenomena in physics, chemistry, and biology. Examples in the physical sciences have included studies of fluid dynamics,[15−18] spin glasses,[19] ferromagnetism,[17] and the Belousov−Zhabotinskii oscillatory reaction.[20−24] Lattice−

gas cellular automata have proven especially effective in treating dynamical systems.[25−31] Biological applications have involved, among others, the dynamics of cardiac conduction,[32] coat markings of animals,[33] characteristics of microtubules,[34,35] fungal branching,[36] and bacterial growth.[37] A review describes some of these latter applications.[38] Recently, Kier and Cheng have developed a visualizable CA model and applied it to studies of water structure,[39] solubility,[40] the hydrophobic effect,[41] dissolution and diffusion of solutes from a solid mass,[42] and partitioning of a solute between immiscible liquids.[43]

THE PRESENT SYSTEM

A first-order kinetics CA program written in the object-oriented C^{++} programming language has been developed that provides a graphic portrayal of cellular automata dynamics. The program allows two-dimensional simulation of the state and transition function rules of cells on a grid. The cell states are identified by different colors. (As many as 14 colors can be used.) The present version of the program runs on IBM-compatible personal computers. Simulations can be stopped for examination at any point and then restarted.

The program graphic utilizes a checkerboard grid of adjacent (tessellated) cells. The size of the grid (number of cells) can be varied. The configuration of the system at any time is defined by the states of all of its cells. At discrete intervals of time, discrete changes in each cell occur according to rules that constitute the state transition functions. The state transition probability rules $P(i,j)$ for transitions from state i to state j are specified in advance by the user and held constant throughout the simulation. Actual outcomes are determined from these probabilities by means of a random number generator. As a result, every simulation run is an independent and unique trial. Fluctuations in the system behavior, an aspect not addressed in the deterministic approach, are accounted for in a natural manner. In each iteration every cell in the system is given an opportunity to change its state. The sequence of choices of the cells is random in an iteration, every cell in the system having its turn.

In addition to the graphic display, the program collects specific data after each cycle in files useful for direct recall and plotting. The data collected may be any of a number of specified *attributes* of the system. For example, one might retain information on the numbers of cells in each of the several allowed states (blue, green, red, ...) as the simulation evolves, or alternatively, one could retain counts of, e.g., blue cells with 0, 1, 2, 3, and 4 adjacent red neighbors. Many attributes are found to have bearing on the physical interpretation of the automaton's behavior.[39−43] The program also contains a plotting routine.

In earlier CA studies of water properties only cell *movement* rules were used.[39−43] In particular, the probability that an object would move to an adjacent empty cell was determined by how many of its neighbor cells were occupied and the natures of the occupants. The present first-order kinetic program, in contrast, requires only *state change* rules. All cells in the system are stationary. Moreover, in the present application cells in the neighborhood of a given cell do not influence its state changes; these changes are governed only by the transition probabilities $P(i,j)$ specified at the beginning of each simulation.
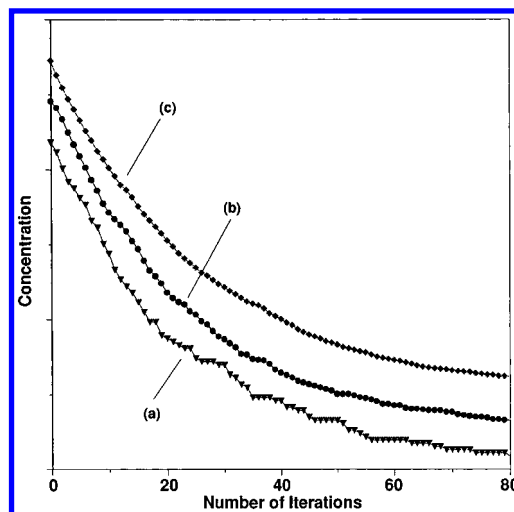

Figure 1. Decay curves (offset) for cellular automata with (a) 100, (b) 400, and (c) 2500 cells. The decay transition probability for a given cell is $P(A,B) = 0.04$/iteration.

RESULTS AND DISCUSSION

In order to demonstrate the utility of cellular automata we have examined several "classic" problems in first-order chemical kinetics. In the following analyses we shall note the characteristics that are unique to the stochastic approach, as well as provide comparison of the results with the those of the deterministic approach. Several features of the CA simulations will be examined by comparing the behaviors in the limits of (a) large grid size (large numbers of cells in the grid), (b) averages of many small-grid results, and (c) single grid fluctuations over long time spans.

1. First-Order Decay. The simple transformation A → B, exemplified by nuclear decay and some isomer transitions, is undoubtedly the best-known example of a first-order process. This is simulated in our CA system by filling an $N \times N$ grid with cells in state A and specifying the transition probability $P(A,B)$. The initial "concentration" of A, $[A]_o$, is designated 1.00. "Time" is specified in units of system iterations (Itn). The results are illustrated in Figure 1 for single trials using 10×10, 20×20, and 50×50 grid sizes and $P(A,B) = 0.04$. The stochastic nature of the process is readily apparent in Figure 1a for the smallest (10×10) grid size, whereas for the largest (50×50) grid size the appearance of the decay curve is almost indistinguishable from that obtained using a deterministic approach. The deterministic first-order rate constant k is directly proportional to (and in the present example, numerically equal to) the state transition probability $P(A,B)$.

Since each run is an independent trial the half-life, $t_{1/2}$ (here represented by the number of system iterations $n_{1/2}$ required for the number of A cells to decrease by half), varies from one run to another. The expected average half-life can be estimated from the deterministic solution $\langle t_{1/2} \rangle = \ln 2/P$. For example, for $P = 0.001$, $\langle t_{1/2} \rangle = 693.1$ iterations. Fluctuations in $t_{1/2}$ present in finite systems (of sufficiently large size) may be expected to display an approximately normal distribution about the mean value with a variance σ^2 which depends inversely on the number of cells (N^2 for an $N \times N$ grid). Thus, the standard error s for $t_{1/2}$ should vary approximately as $1/N$. This was verified using $P(A,B) = 0.001$ and several grid sizes. The results for three series of 99 runs each were (a) 100 cells, $t_{1/2} = 683.7$ (± 96.1) Itn,
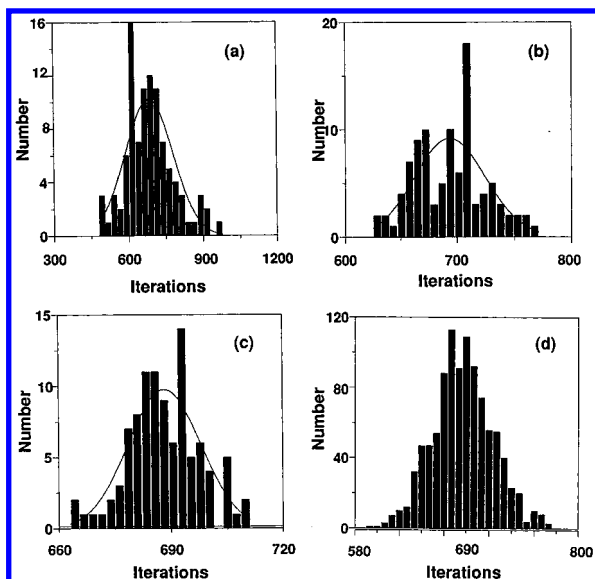
Figure 2. Histograms from 99 trials of the first-order decay half-lives, $t_{1/2}$, of cellular automata with (a) 100 cells, (b) 992 cells, and (c) 10 000 cells. In d the results are shown for 1000 trial runs of a 1024-cell system. Note the changes of scale.

Figure 3. Concentration vs time curves from a single trial run for the first-order equilibrium A $\rightleftharpoons$ B in a 1600-cell system with $P(A,B)$ = 0.05 and $P(B,A)$ = 0.04. The starting concentration of A was 1.00.

(b) 992 cells, $t_{1/2}$ = 693.7 ($\pm$31.4) Itn, and (c) 10 000 cells, $t_{1/2}$ = 688.3 ($\pm$9.7) Itn, where the standard errors are shown in parentheses. The range of $t_{1/2}$ values narrowed strikingly as the system cell size was increased: (a) 100 cells, 479–976 Itn, (b) 992 cells, 625–758 Itn, and (c) 10 000 cells, 663–711 Itn. Histograms showing results for these cases are shown in Figure 2. The figures show a strong resemblence to results obtained in recent "single-molecule" experiments.[44-46]

To further test this feature a sequence of 1000 trial runs using a 32 × 32 = 1024 cell grid was carried out and yielded $t_{1/2}$ = 690.8 ($\pm$30.7) Itn. Four traditional tests of normality (Martinez–Iglewicz, D'Augostino skewness, kurtosis, and omnibus) were satisfied, while a fifth test (Kolmogorov–Smirnov) narrowly rejected normality. A histogram for this example is also shown in Figure 2. (Note the changes in scale for the different cases.)

2. Opposing First-Order Reactions. The equilibrium created by opposing first-order reactions

$$ A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B $$

was next simulated. Ten-run averages for a system with 400 cells were obtained for several sets of $P(A,B)$ and $P(B,A)$ values and a variety of starting concentration ratios. The stochastic equilibrium constant in this case is given by K_{eq} = [B]/[A], in comparison to the deterministic $K_{eq} = k_f/k_r$ = $P(A,B)/P(B,A)$ from the law of mass action. For the case $P(A,B)$ = 0.05, $P(B,A)$ = 0.04 and $[A]_o$ = 1.00, a 10-run trial yielded K_{eq} = 1.27 ± 0.13 (standard deviation), compared with the deterministic value of 1.25. A similar set of 10 runs starting with $[B]_o$ = 1.00 gave K_{eq} = 1.24 ± 0.09. Typical results are illustrated in Figure 3. Repeated tests showed that the final values obtained for K_{eq} were independent of the initial concentrations, as required.

For the present purposes we shall refer to the cellular automaton as *ergodic*[47] if the average obtained for K_{eq} from a large number of individual runs for identical systems is equal to that obtained for a single system observed repeatedly
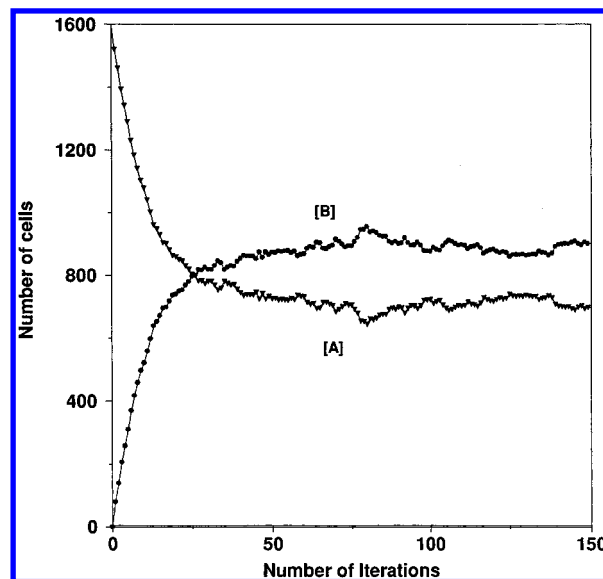
at different times following attainment of equilibrium. To examine this aspect systems of 100 × 100 = 10 000 cells were studied using $[A]_o$ = 1.00, $P(A,B)$ = 0.06 and $P(B,A)$ = 0.03. For the ensemble average $\langle[A]\rangle_{ens}$ the average value of [A] was determined for 1000 trials (in effect separate systems) after 100 iterations, a time judged sufficient for the practical attainment of equilibrium. This was compared with the time-average $\langle[A]\rangle_{time}$ obtained by taking the average of 1000 values of [A] taken at 100 Itn intervals for a single system evolving in time. The values obtained (with standard deviations) were $\langle[A]\rangle_{ens}$ = 0.3335 ± 0.0046 (range 0.3189–0.3506) and $\langle[A]\rangle_{time}$ = 0.3336 ± 0.0047 (range 0.3157–0.3485). They are seen to be in excellent agreement, suggesting that the system is ergodic within our definition. (The system was also ergodic using the more elaborate Kolmogorov–Smirnov two-sample test criterion, under which the difference between the two distributions was insignificant.[48])

3. Consecutive Irreversible Reactions. Systems of two consecutive irreversible reactions,

$$ A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C $$
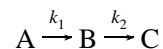
were examined, again utilizing a variety of transition probability values. Several representative stages in a 1600-cell simulation with $k_1 \propto P(A,B)$ = 0.10 and $k_2 \propto P(B,C)$ = 0.05 are shown in Figure 4, with A cells shown as blue, B cells as green, and C cells as red. The simulation kinetics are seen to accurately emulate the traditional deterministic solution found in textbooks.[49,50]

4. The Steady-State Approximation. The deterministic rate laws for multistep reactions are often sufficiently complex that simplifying approximations are invoked to find solutions. The most commonly-invoked approximation, the *steady-state approximation*, holds that the concentration of some intermediate "I" in a reaction remains roughly constant over a considerable time frame; that is,
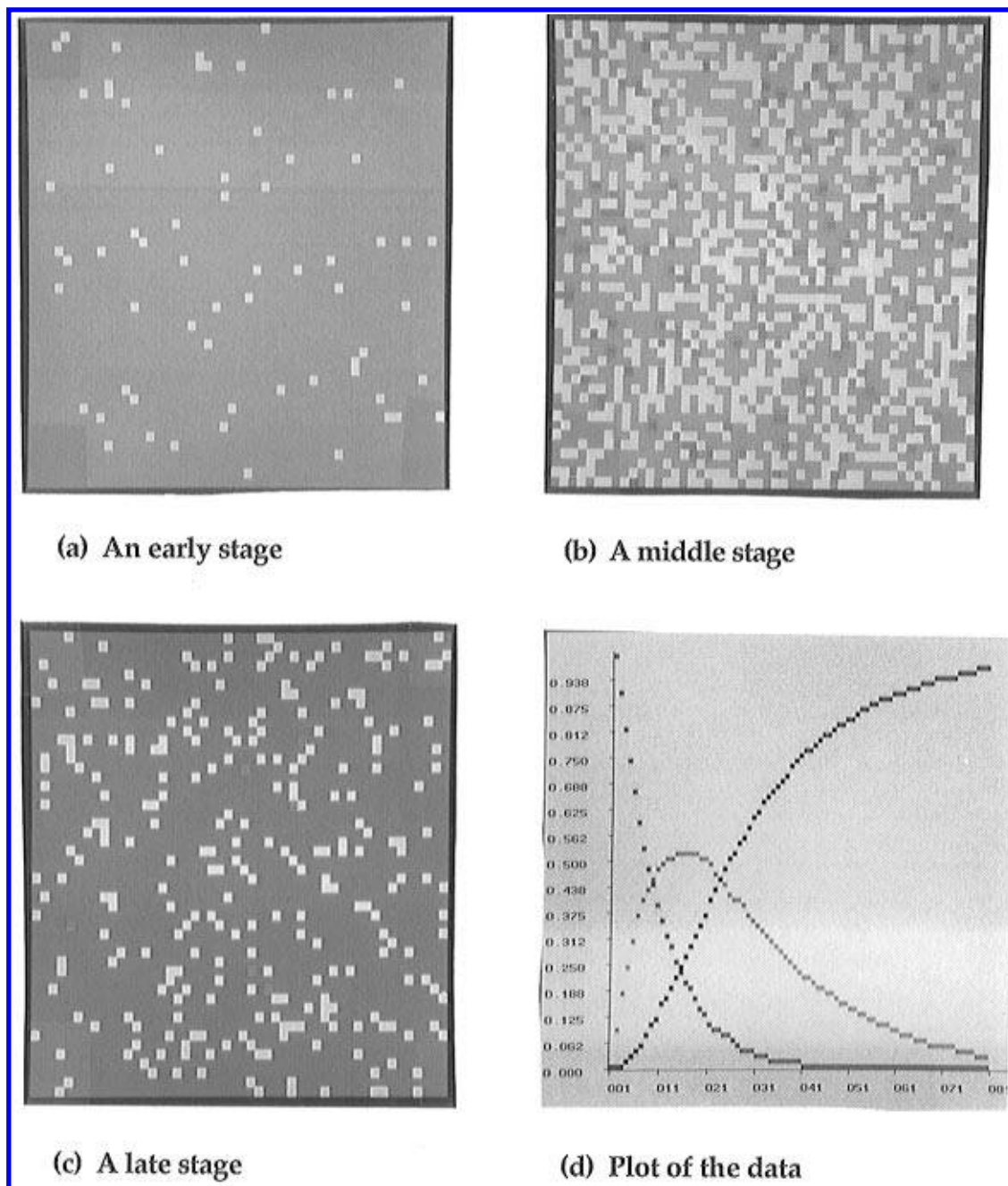
$$ d[I]/dt \approx 0 \tag{1} $$

(a) An early stage

(b) A middle stage

(c) A late stage

(d) Plot of the data

Figure 4. Illustration of system configurations for the two-step reaction A(blue) → B(green) → C(red) (a) at an early stage in the process, (b) at an intermediate stage, and (c) at a late stage. In d a plot of the concentrations of the species vs time is shown.

for a significant period of the reaction. In its common realization the concentration of I is assumed to remain low throughout the reaction.

The previous example, with A → B → C, can be utilized to examine the conditions under which this assumption is valid. If $k_2 \gg k_1$ the conditions required for expression 1 above are reasonably fulfilled. This can be readily demonstrated in the present CA system by setting $P(A,B) = 0.005$ as above, but now with $P(B,C) = 0.100$. The resulting concentration curves for the species A, B, and C are shown in Figure 5. It is clear that (i) the concentration of the intermediate B is approximately constant for a sizable portion of the "reaction", (ii) setting $P(A,B)$ to still lower values would further aid this relation, and (iii) the concentration of C increases in a roughly linear fashion with time under these conditions, as expected. A ratio $k_2/k_1 \geq 20$ allows for

reasonable validity of the steady-state approximation in this example.

We note that reversing the rate ratio, i.e., setting $k_1/k_2 \geq 20$, gives a similar linear increase in the concentration of substance C, but with the important difference that a *high*, yet still roughly constant, concentration of B is maintained during much of the simulation.

5. Rate-Limiting Step. Consider next an example with four consecutive first-order reactions,

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$$
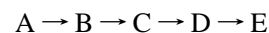
for which one step, i.e., B → C, is much slower than the others. The slowest step is sometimes referred to as the *rate-determining step* of the sequence. This can be illustrated by setting $P(A,B) = P(C,D) = P(D,E) = 0.20$ and setting $P(B,C)$ consecutively to 0.002, 0.004, and 0.006. The
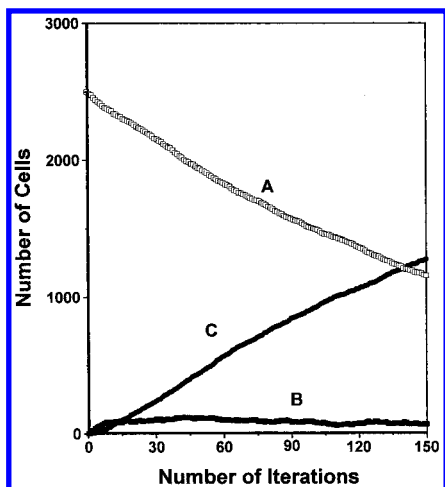
Figure 5. Cell count vs time curves for the sequence A → B → C in a 2500 cell automaton, with $P(A,B) = 0.005$ and $P(B,C) = 0.100$.
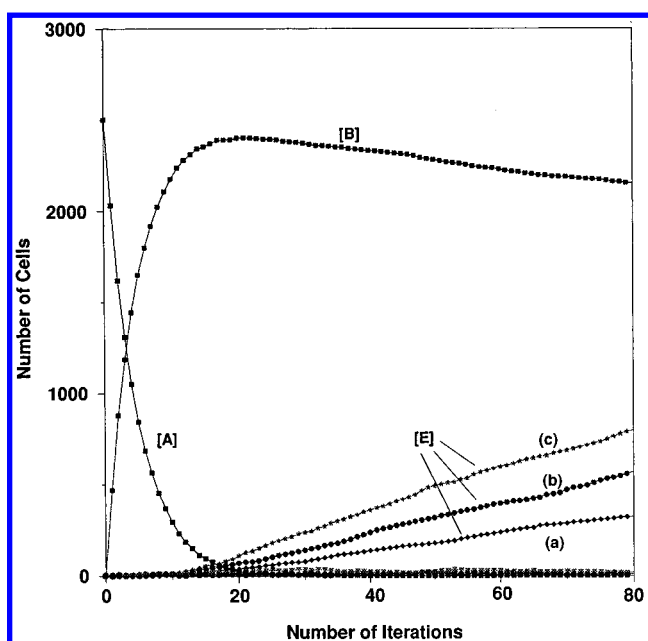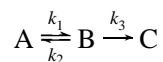

Figure 6. Illustration of a rate-limiting step in the sequence A → B → C → D → E for a 2500-cell automaton. All $P(i,j) = 0.20$ except $P(B,C)$. Curves show the concentration of E for three values of the B → C transition probability: (a) $P(B,C) = 0.002$, (b) $P(B,C) = 0.004$, (c) $P(B,C) = 0.006$.

Figure 7. Concentration vs time curves for a 2500-cell pre-equilibrium simulation with $P(A,B) = 0.2$, $P(B,A) = 0.3$, and $P(B,C) = 0.005$.

Figure 8. Concentration vs time curves for competing reactions A → B and A → C. $P(A,B) = 0.02$ and $P(A,C) = 0.04$.

resulting concentration curves are shown in Figure 6. The approximately linear dependence of product (E) formation on $P(B,C)$ is readily evident. Conversely, reasonable changes in the other rates, such as doubling $P(C,D)$ to 0.4, cause only very minor alterations in the production of E. The CA system also emphasizes the similarity of this example to the results shown previously for the steady-state approximation.

6. Pre-equilibrium. The situation in which two tightly coupled reactions are drained by a loosely coupled reaction,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \overset{k_3}{\rightarrow} C$$

is sometimes termed a pre-equilibrium.[49] The rate of production of C can be approximately expressed as $k_3[B] \approx k_3 K_{12}[A]$, where $K_{12} = k_1/k_2$ is the "equilibrium constant" between A and B. Thus, production of [C] is, in effect,
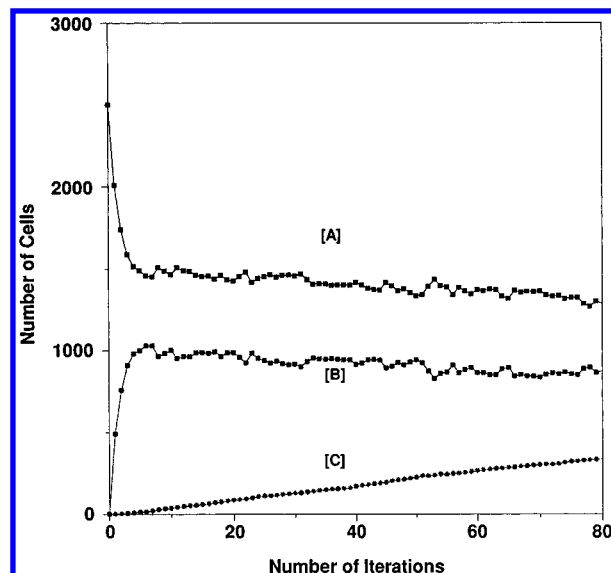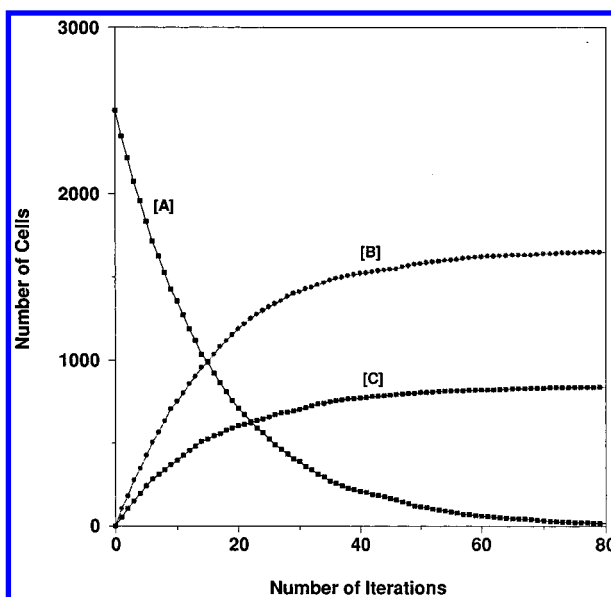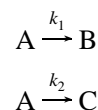
linearly dependent on [A]. This can be illustrated by assigning $P(A,B) = P,(B,A) = 0.2$ and $P(B,C) = 0.004$. The results for this CA system are shown in Figure 7.

7. Parallel Competing Reactions. As a final example we examine the case of two competing reactions,

$$A \overset{k_1}{\rightarrow} B$$

$$A \overset{k_2}{\rightarrow} C$$

The deterministic rate constant for disappearance of A is $k = k_1 + k_2$, and the final ratio [B]/[C] is expected to equal k_1/k_2. Using $P(A,B) = 0.04$ and $P(A,C) = 0.02$, a typical result for a single trial of a $50 \times 50 = 2500$-cell system is illustrated in Figure 8. The ratio [B]/[C] found after 150 iterations for 10 trials with this system varied from 1.947 to 2.090. The average value was 2.004 ± 0.040, in excellent agreement with the deterministic value of 2.00.

CONCLUSIONS

The above examples demonstrate that a suitably structured cellular automaton, exercising only simple local rules based on probabilities, successfully simulates the common processes of first-order chemical kinetics. The automaton model illustrates, in addition, the stochastic variations to be expected in trials employing various numbers of cells, which act as molecular surrogates. Fluctuations in the behaviors of the systems emerge in a natural way as the systems evolve in time. The deterministic solutions are seen clearly to be statistical averages valid only in the limit of large (in numbers of cells) systems. Thus, the cellular automaton model provides an attractive heuristic alternative to the sometimes quite complicated deterministic approach to these problems. Moreover, it represents more closely the actual submicroscopic events that a kinetic model is intended to reproduce.

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