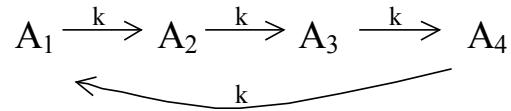


CE 561 Homework 2: (assigned 9/9/09, due 9/14/09)

- (1) Consider the network of 1st order reactions given by



where for simplicity, we have given all four reactions the same rate constant and made all four reactions irreversible (note that a cyclic system of irreversible reactions with identical rate constants would be *extremely* unlikely to occur in practice, but it's a nice problem).

- Write this set of reactions in matrix form (i.e. $\underline{\alpha}A = \underline{0}$)
 - Write the rate equations in terms of the reaction rates in matrix form using the stoichiometric matrix (i.e. $\frac{dC}{dt} = \underline{\alpha}^T \underline{r}$).
 - Write the rate equations in terms of a matrix of rate constants and a vector of concentrations (i.e. $\frac{dC}{dt} = \underline{M}C$). How are the matrices $\underline{\alpha}^T$ and \underline{M} related?
 - Find an analytical solution to the rate equations (for $C_{A_1}(t=0)=C_0$, $C_{A_2}(t=0)=C_{A_3}(t=0)=C_{A_4}(t=0)=0$) using the matrix method discussed in class.
 - If there are i A_1 molecules, j A_2 molecules, and k A_3 molecules in the system at time t , what is the probability that at some very short time later ($t+\Delta t$) there are $j+1$ A_2 molecules? What is the probability that there are $j-1$ A_2 molecules? What is the probability that there are j A_2 molecules?
- (2) Suppose we wanted to model the behavior of populations in a rabbit farm in the same way we have been modeling chemical rate processes. Let N_M be the number of adult male rabbits, let N_F be the number adult female rabbits, and let N_B be the number of pre-pubescent baby bunnies. Suppose we sell baby bunnies (for pets) and adult rabbits (for food), each in proportion to their total population. Then the rate processes might be written in terms of the following list of "reactions"
- $M + F \rightarrow M + F + B$, with $r_1=k_1N_F$
 - $B \rightarrow M$, with $r_2=k_2N_B$
 - $B \rightarrow F$, with $r_3=k_3N_B$
 - $F \rightarrow X$, with $r_4=k_4N_F$
 - $M \rightarrow X$, with $r_5=k_5N_M$
 - $B \rightarrow X$, with $r_6=k_6N_B^2$

Where X as a product indicates that there is no product of that reaction (the rabbit leaves the farm and we no longer keep track of it)

The numerical values of the rate constants for these processes are

$$\begin{aligned}k_1 &= 3.5 \text{ events rabbit}^{-1} \text{ month}^{-1} \\k_2 &= k_3 = 0.15 \text{ events rabbit}^{-1} \text{ month}^{-1} \\k_4 &= 0.1 \text{ events rabbit}^{-1} \text{ month}^{-1} \\k_5 &= 0.5 \text{ events rabbit}^{-1} \text{ month}^{-1} \\k_6 &= 0.1 \text{ events rabbit}^{-2} \text{ month}^{-1}\end{aligned}$$

The "initial conditions" for this problem are that at time = 0, $N_M = 2$, $N_F = 10$, $N_B = 0$. That is, we start with 2 male rabbits, 10 female rabbits, and no baby bunnies.

- (a) Write the rate equations for N_M , N_F , and N_B . Can these differential equations be solved analytically?.
- (b) Write a short computer program (in the language of your choice) that uses Euler's method to solve the rate equations numerically (treating N_M , N_F , and N_B as continuous variables, like we usually do for chemical concentrations). Compute and plot the 'concentrations' from $t = 0$ to whatever time is needed to reach steady state (until they stop changing).
- (c) Write a short computer program that uses kinetic Monte-Carlo methods to simulate the rabbit farm's population over time, treating N_M , N_F , and N_B as integer variables. Run the program several times. Compute and plot the 'concentrations' from $t = 0$ to whatever time is needed to reach steady state (until they stop changing).
- (d) Compare the results of parts (b) and (c), discussing similarities, differences, and the importance of statistical fluctuations for this problem.