

Markov chains (application of systems of linear equations)

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I especially appreciate the part „try to implement the recurrence in Matlab, generate the two sequences of numbers, try to estimate the limits and verify“. Maybe we can only say „think about how would you implement the recurrence in Matlab“ and leave the rest (the work) for the classroom task? I think it might be engaging and also could be a starting point for a discussion. For the „verify part“, we could suggest a task that plays with the fact that a solution to the equation $Px=x$ (fixed point, equilibrium) might be found by solving matrix equation $(P-I)x=0$ with the constraint $x^A + x^B = 1$. What do you think? I think that we can consider this as an application of systems of equations. In fact, there are three equations in two variables.

the case from chemistry rather could fit into such a task instead of being built into the video? I know you had another idea, but this one was really fitting to such a task as well.



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Article...

ChE class and home problems

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

SOLVING CHEMICAL KINETICS PROBLEMS BY THE MARKOV-CHAIN APPROACH

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Imagine the following scene: you are correcting a quiz given to students in your (say) second year chemical kinetics course. You assigned the problem of a homogeneous mixture containing initially 1 mole of species A and 0.2 moles of species B. $A \rightleftharpoons B$ reactions are by no means imaginary; the classical gas-phase reaction between ortho- H_2 and para- H_2 ,¹¹ and the liquid-phase hydrolysis of lactone to γ -hydroxybutyric acid in strong hydrochloric acid solutions¹² are two real-life examples. In every minute, 75 mole % of A are converted to B, and 5% of B converted to A. How many moles of A and B are present in the mixture at one and two minutes after the process has started, and what is the final (equilibrium) composition?

You are trudging your way through a motley collection of answers based on more-or-less successful attempts by your students to set up the conventional differential rate equation and to integrate them somehow. Your boredom threatens to reach unprecedented depths—when suddenly you come across the unexpected. One of your students almost obtained the right answers . . . without writing down a single rate equation.

Congratulations! This student of yours apparently recognized that the reaction process may be interpreted as a Markov chain in the theory of stochastic processes. Composition is considered as a probability (state) vector and the rate constants as transitional



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probabilities; the final composition is given by a straightforward application of the eigenvalue problem in linear algebra. For want of numerical carefulness, the answers are slightly off. Never mind—give this student an A* for leaving behind the conventional, the obvious, the unimaginative!

THE CHEMICAL REACTION AS A MARKOV CHAIN

The key to this off-the-beaten-path approach is that the amounts of species A and B present at the $(n+1)^{\text{st}}$ time unit depend only on their amounts at the n^{th} time unit. Calling the amounts states, we can now say that transition between two consecutive (adjacent) states is independent of transition between any other states. We may think of the transition between states as a probability matrix with its elements given by the rate constants which, in turn, are interpreted as transitional probabilities.

The Markov chain model of the reaction is

$$A(n+1) = 0.25 A(n) + 0.05 B(n) \quad (1a)$$

$$B(n+1) = 0.75 A(n) + 0.95 B(n) \quad (1b)$$

with $A(0) = 1$ and $B(0) = 0.2$. The transition matrix

Chemical Engineering Education

(Markov matrix) is

$$\mathbf{P} = \begin{pmatrix} 0.25 & 0.05 \\ 0.75 & 0.95 \end{pmatrix} \quad (2)$$

and the state vector

$$\mathbf{p}_n = \begin{pmatrix} A(n) \\ B(n) \end{pmatrix} = \mathbf{P}^n \mathbf{p}_0 \quad (3)$$

yields the time-dependent concentrations. Numerically (in moles), the solution vectors after one minute and two minutes are

$$\begin{pmatrix} A(1) \\ B(1) \end{pmatrix} = \begin{pmatrix} 0.25 & 0.05 \\ 0.75 & 0.95 \end{pmatrix} \begin{pmatrix} 1 \\ 0.2 \end{pmatrix} = \begin{pmatrix} 0.26 \\ 0.94 \end{pmatrix}$$

and

$$\begin{pmatrix} A(2) \\ B(2) \end{pmatrix} = \begin{pmatrix} 0.25 & 0.05 \\ 0.75 & 0.95 \end{pmatrix} \begin{pmatrix} 0.26 \\ 0.94 \end{pmatrix} = \begin{pmatrix} 0.112 \\ 1.088 \end{pmatrix}$$

The conventional, and more time-consuming, method is to solve the differential rate equations

$$\frac{dA}{dt} = -0.75A + 0.05B$$

$$\frac{dB}{dt} = 0.75A - 0.05B$$

which yield

$$A(t) = 0.075 + 0.925 \exp(-0.8t)$$

$$B(t) = 1.125 - 0.925 \exp(-0.8t)$$

The equilibrium concentrations are found via the

$$\lim_{n \rightarrow \infty} \mathbf{p}_n = \mathbf{p}^* = \text{const. property of the chain}$$

which implies the relationship

$$\mathbf{P} \mathbf{p}^* = \mathbf{p}^* \quad (4)$$

e.g., an eigenvalue problem with eigenvalue of unity. In our case, Eq. (4) is

$$\begin{pmatrix} 0.25 & 0.05 \\ 0.75 & 0.95 \end{pmatrix} \begin{pmatrix} p_1^* \\ p_2^* \end{pmatrix} = \begin{pmatrix} p_1^* \\ p_2^* \end{pmatrix}$$

which yields an eigenvector

$$\begin{pmatrix} 1 \\ 15 \end{pmatrix}^k$$

where k is an arbitrary real constant. If k is chosen as the "normalizer" value

$$\frac{(A_0 + B_0)}{(1 + 15)} = \frac{1.2}{16}$$

the equilibrium values $A^* = 1.2/16 = 0.075$ mol and $B^* = (1.2)(15)/16 = 1.125$ mol are found immediately.

The attractiveness of the Markov-chain approach increases with the number of reacting components, e.g., the dimensionality of the problem. Suppose that three components A, B, C react in a mixture with

Winter 1993

differential rate equations

$$\frac{dA}{dt} = -0.3A + 0.1B$$

$$\frac{dB}{dt} = 0.2A - 0.3B + 0.1C$$

$$\frac{dC}{dt} = 0.1A + 0.2B - 0.1C$$

with initial composition $A_0 = 1$, $B_0 = 0.6$, and $C_0 = 0.3$ mol. In the Markovian approach

$$\mathbf{p}_n = \begin{pmatrix} 0.7 & 0.1 & 0.0 \\ 0.2 & 0.7 & 0.1 \\ 0.1 & 0.2 & 0.9 \end{pmatrix} \mathbf{p}_{n-1} = \begin{pmatrix} 0.7 & 0.1 & 0.0 \\ 0.2 & 0.7 & 0.1 \\ 0.1 & 0.2 & 0.9 \end{pmatrix}^n \begin{pmatrix} 1 \\ 0.6 \\ 0.3 \end{pmatrix} \quad (5)$$

represents the state of the reaction mixture of each time instant. The eigenvector associated with equilibrium has the elements (1, 3, 7), and $k = 2/11$ is the normalizer yielding the equilibrium concentrations $A^* = 0.1818$, $B^* = 0.5454$, and $C^* = 1.2727$ mol. The handling of the equilibrium state does not require, of course, the solution of the differential rate equations, but the manipulations of the algebraic equation set obtained by equating the concentration derivatives to zero are not simpler than the computation of the eigenvector.

The didactic value of the Markov-chain path of solution lies not only in its simplicity and elegance, but also 1) in demonstrating the power of probability theory in handling *a priori* deterministic problems, and 2) in applying fundamental tenets of linear algebra to tangible physical problems of practical importance. Undergraduate students in engineering usually regard linear algebra as an esoteric nuisance (the student in this story is a rare bird, indeed!); treating chemical kinetics problems with appropriate techniques of linear algebra proves the opposite.

The power of Markovian thinking is much wider than what is presented here. Physics, biology, economics, communications, and computer networks are well-known areas of application. The interested reader will find references 3-5 useful for further exploration.

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43

-1,6094379124341

I steded for -0.8 i exponential (exp)

Exp(-k*t), exp(-k)=0.2 -> k=-ln(0.2) = ln(5)

log(5) i steded for 0.8

Task

Markov chains can be used for solving problems in chemistry, for example in chemical kinetics.

Imagine that we have a homogeneous mixture of two species/components A and

B that react with each other.

At the start of the reaction, there is 1.0 mole of component A and 0.2 moles of component B.

In every minute, 75% of moles of A are converted to B, and 5% of B are converted to A.

We would like to know:

How many moles of A and B are present in the mixture at one minute after the process has started?

How many moles of A and B are present in the mixture at two minutes after the process has started?

How many moles of A and B are present in the mixture at ten minutes after the process has started?

What would be the final composition/stable state/stable equilibrium?

(Implementation inquiry questions:)

How to write/draw the model on paper using mathematics/figures? Is there any way to make use of vectors and matrices?

How to "code" the model in Matlab?

How many iterations did we perform before we thought we can guess the final state/stable solution/equilibrium?

In what other way(s) could we calculate the equilibrium? Is there any way to make use of vectors, matrices and a piece of paper?

Let's have a look at the values we obtained doing iterations. We shall notice that the distances between the states in neighbouring minutes differ, that is, are decreasing in time.

Now imagine that we would like to know how many moles of A and B are present in the mixture after, say, 90 or 150 seconds (1.5 and 2.5 minutes). How could we calculate the state at any time "between the whole minutes"?

Here the students need to use a digital tool, I guess? Should we recommend them to have their matlab or octave ready?

What is the idea behind these questions? Are you going in the direction of eigenvectors? The students does not know this theory yet.

I would say that the direction is "matrix equations" and "operations with vectors and matrices". In particular, are the students able to see that a matrix equation $A*x=x$ can be converted to $A*x - x=0$? If so, would they come up with the idea of "factoring" x and how to do it? If they do, they actually will not necessarily come across the idea of eigenvalues. I did not use any knowledge about eigenvalues to solve the problem via the matrix equation.

In this case you are looking for the set of ODEs?

I want to provoke students in this direction, but not that far. I just would like to see whether they would come up with questions like "How could we pass from (discrete) iterations to a (continuous) process?"

Write the continuous solution: $5^{-(t)}$

Use the idea to find solution to DE at certain points?

$$\frac{dA}{dt} = -0.75 A + 0.05 B$$
$$\frac{dB}{dt} = 0.75 A - 0.05 B$$

$$A' = -\frac{3}{4}A + \frac{1}{20}B$$

$$B' = \frac{3}{4}A - \frac{1}{20}B$$

$$\begin{pmatrix} A' \\ B' \end{pmatrix} = \underbrace{\begin{pmatrix} -\frac{3}{4} & \frac{1}{20} \\ \frac{3}{4} & -\frac{1}{20} \end{pmatrix}}_S \begin{pmatrix} A \\ B \end{pmatrix}$$

$$\det(S - \lambda I) = \begin{vmatrix} -\frac{3}{4} - \lambda & \frac{1}{20} \\ \frac{3}{4} & -\frac{1}{20} - \lambda \end{vmatrix} = \left(\lambda + \frac{3}{4}\right)\left(\lambda + \frac{1}{20}\right) - \frac{3}{80} =$$
$$= \lambda^2 + \left(\frac{3}{4} + \frac{1}{20}\right)\lambda + \frac{3}{80} - \frac{3}{80} = \lambda\left(\lambda + \frac{16}{20}\right) = \lambda(\lambda + 0.8)$$