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.

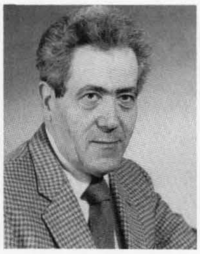
SOLVING CHEMICAL KINETICS PROBLEMS BY THE MARKOV-CHAIN APPROACH

Thomas Z. Fahidy
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

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 $\rightleftarrows$ B reactions are by no means imaginary; the classical gas-phase reaction between ortho-H_2 and para-H_2,[1] and the liquid-phase hydrolysis of lactone to γ-hydroxybutyric acid in strong hydrochloric acid solutions[2] 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 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!



Thomas Z. Fahidy *received his BSc (1959) and MSc (1961) from Queen's University and his PhD (1965) from the University of Illinois (Urbana-Champaign). He teaches courses in applied mathematics to engineering students and conducts research in electrochemical engineering. His major research areas are magnetoelectrolysis and the development of novel electrochemical reactors. He is the author of numerous scientific articles.*

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)st time unit depend only on their amounts at the nth 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

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

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

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

(Markov matrix) is

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

and the state vector

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

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

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

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

which yield

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

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

The equilibrium concentrations are found via the

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

which implies the relationship

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

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

$$\frac{(A_o + B_o)}{(1+15)} = \frac{1.2}{16}$$

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 differential rate equations

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

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

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

with initial composition $A_o = 1$, $B_o = 0.6$, and $C_o = 0.3$ mol. In the Markovian approach

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

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.

REFERENCES

1. Wakao, N., P.W. Selwood, and J.M. Smith, "Low Temperature Ortho-Para Hydrogen Conversion-Kinetic Studies," *AIChE J.,* **8**, 478 (1962)
2. Long, F.A., W.F. McDevit, and F.B. Dunkle, "Salt Effects on the Acid-Catalyzed Hydrolysis of γ-butyrolactone. II. Kinetics and Reaction Mechanism," *J. Phys, and Colloid. Chem.,* **55**, 829 (1951)
3. Cox, D.R., and H.D. Miller, *The Theory of Stochastic Processes,* Chapman and Hall, London (1965, 1970)
4. Rozanov, Y.A., *Probability Theory: A Concise Course,* Dover, New York (1969)
5. Greenberg, M.D., *Advanced Engineering Mathematics,* Prentice Hall, Englewood Cliffs, NJ (1988) ❐