

# STOCHASTIC MODELING OF CHEMICAL PROCESS SYSTEMS

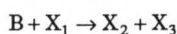
## Part 3: Application

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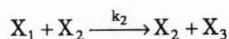
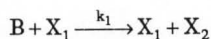
IN THIS FINAL part of our three-part series on stochastic modeling of chemical process systems, the master equation derived in Part II is employed to model a chemically-reacting system. The purpose is two-fold: the first is to demonstrate the application of the master equation, and the second is to show that fluctuations will be negligible in a reacting system where the number of discrete entities (molecules) is large. Nevertheless, this is not always the case for a system with a relatively small population, *e.g.*, a bubbling fluidized-bed combustor for large coal particles. Such a system also is not uncommon at the outset and conclusion of any process; these periods are the most critical from the standpoint of operation, monitoring, and control.

### EXAMPLE CALCULATION WITH THE MASTER EQUATION

For the reaction



its elementary steps can be expressed as



We shall assume that these reactions take place in a well-mixed vessel of volume  $\Omega$  under isothermal conditions. The proper modeling of concentration fluctuations in the system requires knowledge of the elementary (molecular) reaction mechanism. However, this information is not known in many industrially relevant reactions; thus, phenomenological kinetic models are employed [1]. Such phenomenological models, however, are not sufficient to determine the exact nature of the inter-

nal fluctuations.

We shall also assume that the feed stream to the reactor contains only component  $X_1$  and that the system has a mean residence time of  $\tau_s$ . Of the three components involved in the reaction steps,  $X_1$  and  $X_2$  will be variable, while  $B$  is assumed to be held at a constant concentration. Finally, for deriving a stochastic model, it will be assumed that each molecule behaves independently and thus will react with a probability derivable from the rate equations of chemical kinetics [2].

### Rate of Transition Functions

If we define  $N_1$  and  $N_2$  as the numbers of molecules of component  $X_1$  and  $X_2$ , respectively, in the reaction volume, the following rates of transition,  $W_t(n_1, n_2; \xi_1, \xi_2)$ , can be derived [2,3]:

$$W_t(n_1, n_2; 1, 0) = \frac{\Omega C_f N_A}{\tau_s} \quad (1)$$

$$W_t(n_1, n_2; -1, 0) = \frac{n_1}{\tau_s} + \frac{k'_2}{\Omega} n_1 n_2 \quad (2)$$

$$W_t(n_1, n_2; 0, -1) = \frac{n_2}{\tau_s} \quad (3)$$

$$W_t(n_1, n_2; 0, 1) = B k_1 n_1 \quad (4)$$

The first of these is due to the entrance of molecules of  $X_1$  into the reactor; hence,  $\Omega C_f N_A / \tau_s$  is the number of molecules of  $X_1$  entering the reactor per unit time. The second expression, Eq. (2), is due to molecules of  $X_1$  leaving the reactor and to the second chemical reaction. The third, Eq. (3), corresponds to molecules of  $X_2$  leaving the reactor. Finally, the fourth expression corresponds to the first chemical reaction. Note that the  $k'_2$  is the second-order rate constant in terms of molecules instead of moles with units of time (volume · molecules). The rate constant in terms of moles,  $k_2$ , can be obtained by multiplication of  $k'_2$  by the Avogadro number,  $N_A$ .

## Jump Moments

With the aid of Eqs. (9) and (11) in Part II, the jump moments follow directly from Eqs. (1) through (4). These are

$$A_1 = \frac{\Omega C_f N_A}{\tau_s} - \frac{n_1}{\tau_s} - \frac{k_2'}{\Omega} n_1 n_2 \quad (5)$$

$$A_2 = -\frac{n_2}{\tau_s} + B k_1 n_1 \quad (6)$$

$$B_{1,1} = \frac{\Omega C_f N_A}{\tau_s} + \frac{n_1}{\tau_s} + \frac{k_2'}{\Omega} n_1 n_2 \quad (7)$$

$$B_{1,2} = B_{2,1} = 0 \quad (8)$$

$$B_{2,2} = \frac{n_2}{\tau_s} + B k_1 n_1 \quad (9)$$

The application of Eqs. (10) and (12) from Part II followed by Eqs. (14) and (15) from Part II leads to the coefficient matrices of the linearized Fokker-Planck equation governing the fluctuations, *i.e.*,

$$\tilde{A} = [\tilde{A}_{i,j}] = \begin{bmatrix} -\frac{1}{\tau_s} - k_2' \phi_2 & -k_2 \phi_1 \\ B k_1 & -\frac{1}{\tau_s} \end{bmatrix} \quad (10)$$

$$\tilde{B} = [\tilde{B}_{i,j}] = \begin{bmatrix} \frac{C_f N_A}{\tau_s} + \frac{\phi_1}{\tau_s} + k_2 \phi_1 \phi_2 & 0 \\ 0 & \frac{\phi_2}{\tau_s} + B k_1 d_1 \end{bmatrix} \quad (11)$$

## Average Value Equations

The zero-order terms in Eqs. (5) and (6) lead to the following expressions for the average numbers of molecules of the two components:

$$\frac{d}{dt} \langle N_1 \rangle = \frac{\Omega C_f N_A}{\tau_s} - \frac{\langle N_1 \rangle}{\tau_s} - \frac{k_2'}{\Omega} \langle N_1 \rangle \langle N_2 \rangle \quad (12)$$

$$\frac{d}{dt} \langle N_2 \rangle = -\frac{\langle N_2 \rangle}{\tau_s} + B k_1 \langle N_1 \rangle \quad (13)$$

Dividing both sides of these expressions by  $\Omega N_A$  results in the familiar rate equations for reactions in a well-mixed reactor in terms of molar concentrations

$$\frac{dC_1}{dt} = \frac{1}{\tau_s} (C_f - C_1) - k_2 C_1 C_2 \quad (14)$$

$$\frac{dC_2}{dt} = -\frac{1}{\tau_s} C_2 + B k_1 C_1 \quad (15)$$

## Covariances

In addition to the expressions for the average concentrations, the stochastic model also yields expressions

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for the concentration fluctuations. The coefficient matrices, Eqs. (10) and (11), are employed in conjunction with Eq. (23) in Part II for this purpose.

When we divide both sides of the resultant expressions by  $N_A^2$ , we obtain the following expressions in terms of molar concentrations:

$$\begin{aligned} \frac{d}{dt} \text{Var}[C_1] &= -2 \left( k_2 C_2 + \frac{1}{\tau_s} \right) \text{Var}[C_1] \\ &\quad - 2 k_2 C_1 \text{Cov}[C_1, C_2] + \frac{1}{\Omega N_A} \left( \frac{C_f}{\tau_s} + \frac{C_1}{\tau_s} + k_2 C_1 C_2 \right) \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{d}{dt} \text{Cov}[C_1, C_2] &= - \left( \frac{2}{\tau_s} + k_2 C_2 \right) \text{Cov}[C_1, C_2] \\ &\quad - k_2 C_1 \text{Var}[C_2] + B k_1 \text{Var}[C_1] \end{aligned} \quad (17)$$

$$\frac{d}{dt} \text{Var}[C_2] = 2 B k_1 \text{Cov}[C_1, C_2] - \frac{2}{\tau_s} \text{Var}[C_2] + \frac{1}{\Omega N_A} \left( \frac{C_2}{\tau_s} + B k_1 C_1 \right) \quad (18)$$

This set of coupled differential equations can be solved for the covariance and variances of the fluctuations. For our purposes, it suffices to note that the resultant expressions will be proportional to  $(\Omega N_A)^{-1}$ . Since  $N_A \approx 10^{24}$ , we can safely conclude that unless  $\Omega$  is very small ( $\approx 10^{-24}$ ), the concentration fluctuations will have a standard deviation in the order of  $10^{-12}$  mol/volume. Such fluctuations, being imperceptible to most, if not all, instruments commonly employed in practice, must be considered negligible.

## Correlation Functions

According to Eq. (25) in Part II, the expressions for the auto- and cross-correlation functions are, respectively

$$\frac{d}{d\tau} K_{i,1}(\tau) = - \left( k_2 C_2 + \frac{1}{\tau_s} \right) K_{i,1}(\tau) - k_2 C_1 K_{i,2}(\tau), \quad i=1,2 \quad (19)$$

$$\frac{d}{d\tau} K_{i,2}(\tau) = B k_1 K_{i,1}(\tau) - \frac{1}{\tau_s} K_{i,2}(\tau), \quad i=1,2 \quad (20)$$

The initial conditions for these equations are the steady-state covariances. Since these are proportional

to  $(\Omega N_A)^{-1}$ , so will be the correlation functions. The real parts of the eigenvalues for the system of equations, Eqs. (19) and (20), are negative and, most important, functions of the macroscopic rate constants. If the fluctuations were measurable, it would be possible to calculate the rate constants from *steady-state* experiments. However, this is precluded in the chemically-reacting system under consideration because of the immeasurability of fluctuations due solely to the stochastic combination of individual molecules.

## CONCLUDING REMARKS

We have seen that for a Markovian system, where the rates of transition can be formulated, the master equation can be solved approximately for the means and correlation functions of the random variables of interest. Thus it is possible to study the effects of stochastic kinetics on the evolution of discrete populations and on the behavior of the system. This is impossible to accomplish by the conventional deterministic approach that leads to equations only for the means.

The master equation with the attendant System Size Expansion offers advantages over other stochastic formulations. For example, we have seen that the well-known problem of coupling arises between moments of differing orders for a nonlinear system. In most formulations this problem is circumvented by assuming independence among random variables or by resorting to an *ad hoc* procedure. The System Size Expansion follows a more rational pathway. Its power series expansion retains a linear coupling between the means and fluctuating components of the random variables—a coupling ignored or distorted when an *ad hoc* approach is used. In a system where the System Size Expansion is not applicable, the majority of the *ad hoc* procedures are also invalid, and the system is best handled by a simulation procedure, *e.g.*, the Monte-Carlo method.

The magnitude of internally-generated fluctuations has been found to decrease as the number of independent entities increases. This, in turn, has led us to conclude that internal fluctuations due to molecular interactions in a chemically-reacting system are negligible. Nevertheless, it does not imply that the fluctuations in a molecular system will be negligible in general. Indeed, all systems are molecular, but fluctuations are often present. Therefore, the key to modeling fluctuations is the proper identification of their sources.

It is worth noting briefly that the auto- and cross-correlation functions have characteristic time constants which are functions of the macroscopic rate constants.

This observation should be of interest to the experimentalist wishing to determine the constants since the correlation functions are measured for systems operating at steady-state. It is known in physics as the fluctuation-dissipation theorem and is used in measuring various quantities, including diffusion coefficients.

In this series of articles we have concentrated on the stochastic modeling of internal fluctuations in systems amenable to a description involving a stochastic population balance. Another important area of stochastic modeling involving external fluctuations, *i.e.*, fluctuations generated by the environment of the system, is best described by stochastic differential equations that have not been discussed here. The reader will find details on the formulation and solution of model equations for external noise systems in the monographs by van Kampen [2], Gardiner [4], and Horsthemke and Lefever [5]. The last gives an excellent introductory treatment of the effects of multiplicative (noise terms appearing in the governing equations multiplied by the dependent variables) and additive noise in single variable systems. It is shown that additive noise does not change the steady-state solution diagram in single variable systems (all stable and unstable solutions exist at the same parameter values), whereas multiplicative noise can lead to an even richer steady-state solution diagram. New solution branches are generated as the noise intensity increases. Such behavior is known as a “noise induced transition” to emphasize its dependency on the presence of external multiplicative noise.

As remarked at the outset of this series, systems with stochastic components are prevalent in chemical engineering. Currently, several excellent treatises on stochastic modeling stressing physical and chemical systems are available [2,4,5]. These sources are highly recommended to those wishing to expand their knowledge of the subject. In addition, we feel that it is necessary to obtain at least a rudimentary understanding of probability theory, random variables, and stochastic processes as presented in classical treatises such as Feller [6], Karlin and Taylor [7], or, for the more mathematically inclined, Gihman and Skorohod [8]. The reader interested in stochastic differential equations will find an understandable but rigorous presentation in the monograph by Arnold [9]. The introduction of stochastic modeling concepts into basic chemical engineering education is an important step in furthering the ability of chemical engineers to understand the complex systems they frequently encounter. The wide availability of readable, well-written material on stochastic modeling in the modern literature offers an excellent opportunity for chemical engineers to incorporate new methods and fresh

ideas into the modeling of chemical process systems.

## ACKNOWLEDGEMENTS

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## NOTATION

$A_i$	first jump moment
$\tilde{A}_{i,j}$	coefficient in expansion of $\tilde{A}_i$
$B$	concentration of component B
$B_{i,j}$	second jump moment
$\tilde{B}_{i,j}$	$B_{i,j} / \Omega$
$\text{Cov}[C_i, C_j]$	$\langle C_i C_j \rangle - \langle C_i \rangle \langle C_j \rangle$ , covariance of $C_i$ and $C_j$
$C_f$	feed concentration of component $X_1$
$C_1$	concentration of component $X_1$
$C_2$	concentration of component $X_2$
$k_1, k_2$	reaction rate constants
$k_2'$	reaction rate constant in units of molecules
$K_{i,j}(t)$	correlation matrix defined for $C_i$ and $C_j$ as $\langle C_i(0)C_j(\tau) \rangle - \langle C_i(0) \rangle \langle C_j(\tau) \rangle$
$N_A$	Avogadro number
$N_j$	number of molecules of component j
$\langle N_j \rangle$	expected value of random variable $N_j$
$W_t(\{n\}_0, \{n\}_1)$	rate of transition from state $\{n\}_0$ to state $\{n\}_1$

**Greek Letters**

$\xi_i$	magnitude of change in random variable $N_i$
$\tau_s$	mean residence time
$\phi_i$	deterministic variable corresponding to macroscopic behavior of $N_i$
$\Omega$	system volume

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## REVIEW: Polymer Chemistry

Continued from page 153.

really descriptive since the authors seek to treat an extremely large fraction of *polymer science* rather than focussing on the narrower topic of *polymer chemistry*. It would be difficult to have included significant computational problems in the present text because the treatment is highly qualitative. Perhaps because of my chemical engineering bias, some actual examples worked out in detail would have been attractive. For example, condensation and free radical polymerization systems are important enough to merit such treatment even in an overview book such as this.

The references given at the end of the chapters are good, and, in fact, are some of the classics in the various areas. Most of the references are rather old, with only a sprinkling of new sources. While this is not a particular problem for an introductory text, it certainly does not reflect the current literature in a way needed for an introductory graduate (or even a more advanced undergraduate) course.

While the light, easily-read approach is ideal for many of the topics discussed in such an introductory text, some topics might have benefitted from a detailed treatment in order to give the student more than a broad-brush appreciation of their importance to the modern polymer field. It is likely that many instructors would feel the need to supplement the material in the areas of 1) polymer physical properties and their relationship to structure, 2) thermal methods of analysis (DSC, TGA, etc.), and 3) reaction kinetics for condensation and free radical systems. Alternatively, of course, one could direct the student to the original references given at the end of the chapters to obtain sufficient detail to have a true appreciation for these principles. If there is any topic which comes close to being missed, it is the important area of polymer-solvent and polymer-polymer thermodynamics. Although the topic of solubility of polymers in solvents is mentioned, the treatment and importance of solution thermodynamics is given practically no coverage.

The authors indicate that the book could be covered in a normal semester or in two quarter periods, and this seems reasonable. Even with supplemental information and exercises given in the areas noted above, the easily-read style and frequent use of drawings make the material easy to read and to understand. Even if some of the more technological topics covered in the last 40% of the book are not discussed in class, they make useful reading for a student seeking an overview of the field. □