ChE classroom

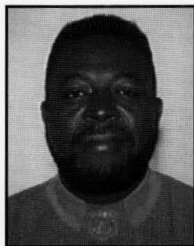
ON USING A BOUNDARY PERTURBATION TO LINEARIZE A SYSTEM OF NONLINEAR PDEs

N. W. Loney
New Jersey Institute of Technology • Newark, NJ 07102

While a mathematical-methods course in graduate chemical engineering programs is a much-needed vehicle for training students in formal analysis, a large part of the course time is expended in bringing all the students up to a common mathematical-maturity level. Although students successfully pass the course, they often leave with the opinion that applications problems can only be solved by using a computer. This may be true in most cases, but some modified version of a difficult problem can be analyzed using the linear theories discussed in class and can provide valuable insight into the phenomena being studied. In order to convince students of the value of this approach, connections must be made with applications problems. One way to demonstrate how such connections can be made is given below.

BACKGROUND

Low-pressure chemical vapor deposition (LPCVD) processes are currently popular methods to produce thin solid films in the microelectronics industry. Of the numerous types of LPCVD processes, the multiwafer hot-wall process is one of the most economical and is widely used in production and developmental reserarch facilities. Currently, the design and operation of the hot-wall process is done mostly through trial and error. For those who can afford the expense, large numbers of experiments are conducted to develop empirical models that are then used to optimize the process.[1] The following is a problem taken from the process of chemical vapor deposition (CVD) in a hot-wall reactor.



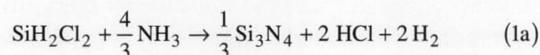
***Norman W. Loney** is Assistant Professor of Chemical Engineering at New Jersey Institute of Technology. He has studied chemical engineering at NJIT and applied mathematics at Courant Institute of Mathematical Science. In addition, Dr. Loney has practical experience in process development, process design, and inplant engineering.*

PROBLEM STATEMENT

Consider a cylindrical tube that is uniformly heated from the outside. Inside, a pyrolyzable gas flows at a given set of flow conditions. The inside tube geometry consists of a set of circular disks placed vertically and equally spaced along the cylinder axis (see Figure 1). These disks are supported in such a way that their axes coincide with that of the cylinder. Gas flows around the disks (through the annulus formed by the disks and cylinder) by convection, while material transfer between the disks is dominated by diffusion. Simultaneous with the mass transfer are chemical reactions, primarily on the surface of the circular disks, that form the desired deposit. One is interested in determining a reasonable concentration profile, given that the surface reaction rate is

$$\frac{k_1 C_A C_B}{1 + k_2 C_A + k_3 C_B} (\text{gmol cm}^{-2} \text{s}^{-1}) \tag{1}$$

where C_A and C_B are concentration of reactant and carrier gas, respectively. For example, if the expected overall reaction is



$$SiH_2Cl_2 + \frac{4}{3} NH_3 \rightarrow \frac{1}{3} Si_3N_4 + 2\,HCl + 2\,H_2 \tag{1a}$$

then species A is SiH_2Cl_2 and B is NH_3. Note that species B can actively participate in the chemical reaction, but C_B must be considerably larger than C_A for it to be qualified as carrier gas.

Equation (1) is typical of the surface rate expressions used in CVD[1-5] systems and can be reduced to

$$\text{Rate} = \frac{k_1 C_A C_{tot}}{K + K' C_A} \tag{2}$$

© Copyright ChE Division of ASEE 1996

Although students successfully pass the [mathematical methods] course, they often leave with the opinion that applications problems can only be solved by using a computer. This may be true in most cases, but some modified version of a difficult problem can be analyzed using the linear theories discussed in class and can provide valuable insight into the phenomena being studied.

where

$$K = 1 + k_3 C_{tot} \tag{3}$$

$$K' = k_2 - k_3 \tag{4}$$

and C_{tot} is the total concentration of species A and B. Also, due to the abundance of species B in the system and the small amount of A that is consumed in a given run, C_{tot} remains relatively constant.

Before continuing, it is important to acknowledge some of the other simplifying assumptions that are made, such as:

- *Gas phase kinetics are neglected*
- *Isothermal condition exists in the reactor*
- *Steady state prevails*
- $C_A << C_{tot}$
- *The wafers are located perfectly axisymmetric with the cylinder*
- *Deposits on the wafer support are neglected*

In order to initiate a solution, connections are to be made between the equation of continuity and the simplifying assumptions. It should be pointed out to the students that as an alternate procedure, the final differential equation can be derived directly from material balance considerations for this system. It should also be noted that fewer simplifying assumptions are usually needed to obtain numerical results (solutions obtained by programmed numerical analysis). But while it is an attractive feature, this approach requires great skill and experience both in numerical analysis and in the particular applications area. Interestingly enough, one way to develop such needed skill and experience is through analytical solution of a modified version of the problem under consideration.

SOLUTION

Following application of the assumptions to the continuity equation and employing constant mass density and diffusion coefficient, we get the differential equation

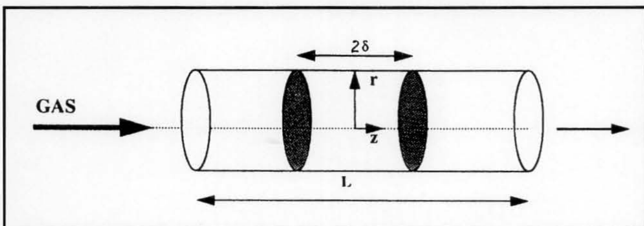


Figure 1. CVD reactor configuration

$$\frac{1}{r}\frac{\partial}{\partial r}\frac{(r\partial C_A)}{\partial r} + \frac{\partial}{\partial z}\frac{(\partial C_A)}{\partial z} = 0 \tag{5}$$

with r and z being respectively the radial and axial coordinates as shown in Figure 1. Equation (5) is subject to the boundary conditions of

$$\frac{\partial C_A}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{6}$$

$$\frac{\partial C_A}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{7}$$

$$C_A(R_w, z) = C_{Ab_i}; \quad 0 < z < \delta \tag{8}$$

and

$$-D_{AB}\frac{\partial}{\partial z}C_A = \frac{k_1 C_A C_{tot}}{K + K' C_A} \quad \text{at} \quad z = \delta \tag{9}$$

In Eq. (8), C_{Ab_i} is the bulk concentration at the ith interwafer region. This quantity (C_{Ab_i}) is a function of the axial coordinate and decays as the reactor exit is approached. But at the ith interwafer region its value is assumed to be relatively constant since wafer spacings are typically small.[6]

It is now convenient to recast the problem in dimensionless form by making use of the following:

Let

$$\frac{C_A(r,z)}{C_{Ab_i}} = F(\xi, \zeta) \tag{10}$$

with

$$\xi = \frac{r}{R_w} \qquad \zeta = \frac{z}{\delta} \tag{11,11a}$$

Then Eqs. (5-9) become

$$\frac{-1}{a^2}\frac{\partial^2 F}{\partial \zeta^2} = \frac{\partial^2 F}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial F}{\partial \xi} \tag{12}$$

$$\frac{\partial F}{\partial \zeta} = 0 \quad \text{at} \quad \zeta = 0 \tag{13}$$

$$\frac{\partial F}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0 \tag{14}$$

$$F(1, \zeta) = 1 \tag{15}$$

$$\frac{-D_{AB}C_{Ab_i}}{\delta}\frac{\partial F(\xi, 1)}{\partial \zeta} = \text{Rxn rate (heterogeneous)} \tag{16}$$

respectively, where

$$a = \frac{\delta}{R_w} \tag{17}$$

Equation (6) or (13) is derived from the assumption that the coordinate system being used is symmetric with respect to z. The condition that species C_A is finite at r=0 is conveniently expressed by Eq. (7) or (14). Equation (8) or (15) simply describes the concentration of species A at that interwafer region. Equation (9) or (16) states that the flux of species A to a wafer surface is balanced by the surface reaction there. This latter boundary condition, Eq. (9) or (16), allows for some novelty in CVD modeling—in our case, a **boundary perturbation.**

MOTIVATION FOR PERTURBATION

Upon examining Eqs. (5) through (9) or (12) through (16), we see that the major obstacle to application of separation of variables directly occurs in Eq. (9) or (16). The right-hand side of the latter equations is a rational function. This quantity can be represented by a convergent power series in an appropriate region. For example, two possibilities for Eq. (2) are

$$\text{Rate} = k_0^* - k_0^*\left(\frac{K'}{K}C_A\right)^{-1} + k_0^*\left(\frac{K'}{K}C_A\right)^{-2} - \ldots \tag{2a}$$

valid for

$$\frac{K'C_A}{K} > 1$$

with

$$k_0^* = \frac{k_1 C_{tot}}{k_2 - k_3} \tag{2b}$$

or

$$\text{Rate} = \frac{k_1 C_A C_{tot}}{K}\left[1 - \frac{K'C_A}{K} + \left(\frac{K'C_A}{K}\right)^2 - \ldots\right] \tag{2c}$$

valid for

$$\frac{K'C_A}{K} < 1$$

By recasting Eq. (2) in its power series form we are able to render the system of differential equations linear. That is, we seek a general power series representation of the reaction rate equation and modify the system as demonstrated below.

Considering the heterogeneous reaction rate expression to be

$$\text{Rate} = k_0 C_{Ab_i}\left(1 + \varepsilon F + \varepsilon^2 F^2 + \varepsilon^3 F^3 + \cdots\right) \tag{18}$$

where

$$F = F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \cdots \tag{19}$$

with

$$\varepsilon = \frac{(k_2 - k_3)C_{A0}}{1 + k_3 C_{tot}} < 1 \tag{20}$$

Eq. (20) is derived through comparison with Eqs. (2a) and (2c). Then, substituting Eqs. (18) and (19) into Eqs. (12) through (16) results in

$$-\frac{1}{a^2}\left(\frac{\partial^2 F_0}{\partial \zeta^2} + \varepsilon\frac{\partial^2 F_1}{\partial \zeta^2} + \varepsilon^2\frac{\partial^2 F_2}{\partial \zeta^2} + \cdots\right)$$
$$= \frac{\partial^2 F_0}{\partial \xi^2} + \varepsilon\frac{\partial^2 F_1}{\partial \xi^2} + \varepsilon^2\frac{\partial^2 F_2}{\partial \xi^2} + \cdots + \frac{1}{\xi}\left(\frac{\partial F_0}{\partial \xi} + \varepsilon\frac{\partial F_1}{\partial \xi} + \varepsilon^2\frac{\partial F_2}{\partial \xi} + \cdots\right) \tag{21}$$

$$\frac{\partial F_0}{\partial \zeta} + \varepsilon\frac{\partial F_1}{\partial \zeta} + \varepsilon^2\frac{\partial F_2}{\partial \zeta} + \ldots = 0 \quad \text{at} \quad \zeta = 0 \tag{22}$$

$$\frac{\partial F_0}{\partial \xi} + \varepsilon\frac{\partial F_1}{\partial \xi} + \varepsilon^2\frac{\partial F_2}{\partial \xi} + \ldots = 0 \quad \text{at} \quad \xi = 0 \tag{23}$$

$$F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \cdots = 1 \quad \text{at} \quad \xi = 1 \tag{24}$$

$$-\frac{D_{AB}C_{Ab_i}}{\delta}\left(\frac{\partial F_0}{\partial \zeta} + \varepsilon\frac{\partial F_1}{\partial \zeta} + \varepsilon^2\frac{\partial F_2}{\partial \zeta} + \cdots\right)$$
$$= k_0 C_{Ab_i}\left[1 - \varepsilon\left(F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \cdots\right) + \varepsilon^2\left(F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \ldots\right)^2 + O\left(\varepsilon^3\right)\right] \tag{25}$$

Equating like powers of ε, we get

ε^0:

$$-\frac{1}{a^2}\frac{\partial^2 F_0}{\partial \zeta^2} = \frac{\partial^2 F_0}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial F_0}{\partial \xi} \tag{26}$$

$$\frac{\partial F_0(0,\xi)}{\partial \zeta} = 0 \tag{27}$$

$$\frac{\partial F_0(\zeta,0)}{\partial \xi} = 0 \tag{28}$$

$$F_0(\zeta,1) = 1 \tag{29}$$

$$-\frac{D_{AB}C_{Ab_i}}{\delta}\frac{\partial F_0}{\partial \zeta} = k_0 C_{Ab_i} \quad \text{at} \quad \zeta = 1 \tag{30}$$

ε:

$$-\frac{1}{a^2}\frac{\partial^2 F_1}{\partial \zeta^2} = \frac{\partial^2 F_1}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial F_1}{\partial \xi} \tag{31}$$

$$\frac{\partial F_1(0,\xi)}{\partial \zeta} = 0 \tag{32}$$

$$\frac{\partial F_1(\zeta,0)}{\partial \xi} = 0 \tag{33}$$

$$F_1(\zeta,1) = 0 \tag{34}$$

$$\frac{D_{AB}C_{Ab_i}}{\delta}\frac{\partial F_1}{\partial \zeta} = k_0 C_{Ab_i} F_0 \quad \text{at} \quad \zeta = 1 \tag{35}$$

$$\varepsilon^2: \quad -\frac{1}{a^2}\frac{\partial^2 F_2}{\partial \zeta^2} = \frac{\partial^2 F_2}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial F_2}{\partial \xi} \tag{36}$$

$$\frac{\partial F_2(0,\xi)}{\partial \zeta} = 0 \tag{37}$$

$$\frac{\partial F_2(\zeta,0)}{\partial \xi} = 0 \tag{38}$$

$$F_2(\zeta,1) = 0 \tag{39}$$

$$-\frac{D_{AB}C_{Ab_i}}{\delta}\frac{\partial F_2}{\partial \zeta} = k_0 C_{Ab_i}\left(F_0^2 + F_1\right) \tag{40}$$

The continuation of this process is possible up to any desired power of ε. Note that by this process, an otherwise nonlinear system is reduced to a set of linear problems. Solving each of the above linear systems, we obtain

$$F_0 = 1 - \frac{2\delta k_0}{aD_{AB}}\sum_{n=0}^{\infty}\frac{J_0(\alpha_n\xi)\cosh(a\alpha_n\zeta)}{\alpha_n^2 \sinh(a\alpha_n)J_1(\alpha_n)} \tag{41}$$

$$J_0(\alpha_n) = 0 \tag{42}$$

$$F_1 = \frac{2\delta k_0}{a^2 D_{AB}}\sum_{n=0}^{\infty}\frac{\frac{\delta k_0}{D_{AB}}\cosh(a\alpha_n) - a\alpha_n \sinh(a\alpha_n)J_0(\alpha_n\xi)\cosh(a\alpha_n\zeta)}{\alpha_n^3 \sinh^2(a\alpha_n)J_1(\alpha_n)} \tag{43}$$

$$F_2 = \sum_{n=0}^{\infty} Q_n J_0(\alpha_n\xi)\cosh(a\alpha_n\zeta) \tag{44}$$

with

$$Q_n = \frac{-2\frac{\delta k_0}{D_{AB}}\int_0^1 F_0^2 \xi J_0(\alpha_n\xi)d\xi}{a\alpha_n \sinh(a\alpha_n)J_1^2(\alpha_n)} - \frac{4\left(\frac{\delta k_0}{aD_{AB}}\right)^2\int_0^1 F_1 \xi J_0(\alpha_n\xi)d\xi}{a\alpha_n \sinh(a\alpha_n)J_1^2(\alpha_n)} \tag{45}$$

where J_0 and J_1 are Bessel functions of the first kind of order zero and one respectively.

The first order approximation F_0 is sufficient to describe the concentration profile of interest. Also note that Eq. (18) expresses a general form of the two possible power series expansions of Eq. (2).

Equation (41) was tested in the prediction of silicon nitride deposition data with reasonable results.[6]

REFERENCES

1. Badgwell, T.A., T.F. Edgar, and I. Trachtenberg, *J. Electrochem. Soc.,* **139**, 524 (1992)
2. Collingham. M.E., and R.L. Zollars, *J. Electrochem. Soc.,* **136**, 787 (1989)
3. Hitchman, M.L., J. Kane, and A.E. Widmer, *Thin Solid Films,* **59**, 231 (1979)
4. Roenigk, K.F., and K.F. Jensen, *J. Electrochem. Soc.,* **134**, 1777 (1987)
5. Kuiper, A.E.T., C.J.H. Van den Brekel, J. de Groot, and G.W. Veltkamp, *J. Electrochem. Soc.,* **129**, 2288 (1982)
6. Loney, N.W., and C.R. Huang, *Thin Solid Films,* **226**, 15 (1993) ❐

REVIEW: Hazardous Waste Management

Continued from page 19.

100-200 new students in the introductory course each year, and as a result we eventually introduced a full MS in HWM, with over thirty required and elective courses. We developed a separate, in-depth course in each of the Wentz chapters and subtopics, outgrowing much of the text. Moreover, the text's data and examples had become dated. So we switched texts, despite the excellent material contained in many chapters and the presentation from the chemical engineer's perspective. We therefore looked forward to the second edition.

Clearly, most students will take only a single course in this field; hence, there is a need for a broad-based text covering the entire subject. The second edition of *Hazardous Waste Management* fits that need well. Wentz provides an overview of all the major topics that should be addressed in HWM.

A major strength of the revised text is its comprehensive coverage within a reasonable number of pages. Another strength is its hard-hitting chemical engineering approach to the technical treatment and remediation subject areas. A major asset is the case studies of many of the major chemical tragedies that have driven federal law development, allowing the student to gain a sense of the field's history as well as its technical requirements. The second edition also groups topics in a more logical order, such as merging toxicology with risk assessment, landfills with injection well disposal, while giving other areas, such as biological treatment, a separate chapter.

The new material in environmental auditing and site assessment and the enhanced technical material in site remediation are major positive additions to the second edition. Likewise, the addition of problems to the technical chapters improves the text significantly as a teaching tool.

Weaknesses of the text include the aged data in Chapter 1, the brevity of the toxicology and environmental auditing sections, and the absence of the OSHA perspective and statistical considerations of data, none of which are serious drawbacks for the student who will take several courses in the field. The international environmental examples provided will increase the students' global awareness, but are largely out of context as they follow discussions of US law.

In summary, the Wentz text led the field since it was first published in 1989; the revised second edition is greatly improved and is a sound choice for a course to round out the background of most chemical engineers. It is also a good choice for an introductory course for a wide range of disciplines with interest in the field. ❐