Diffusion-Convection-Reaction in Multicomponent Mixtures

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We analyze the mathematical structure of a multicomponent reactive mixture in a plug flow reactor with axial diffusion. Quasilinearity of the kinetic equation assuming "uniformity" does not carry over to the second-order equations when diffusion is considered and a perturbation expansion method needs to be developed. Perturbation around the limit of a CSTR is regular, which leads to nonhomogeneous second-order differential equations containing no unknown kinetic term, so that the procedure cascades down to the solution of the CSTR problem. Perturbation around the PFR problem is singular, but the inner (boundary layer) solution is easy. The outer solution leads to a series of integro-differential equations, which can be reduced to complete Volterra integral equations of the second kind; these are known to admit unique solutions. A formal approach to finding these solutions is discussed.

Introduction

After the pioneering works of Wei (1962) and Aris and Gavalas (1966) in the 60s, there has recently been a renewed interest in the chemical kinetics in multicomponent mixtures (Sapre and Krambeck, 1991; Astarita and Sandler, 1991). The *kinetics* in such mixtures have been elucidated at least for the special case where the kinetics are "uniform," in the sense discussed by Astarita and Ocone (1988) and by Aris and Astarita (1989a). Aris and Astarita (1989b) and Astarita (1990) have remarked that results of the same kind would be of interest in the case of higher-order differential equations, such as those which arise when diffusion interacts with chemical kinetics. In this article, the general mathematical architecture of such problems is discussed in some detail.

In principle, the difficulty to be overcome is the same one discussed by Astarita and Ocone (1993a): while the assumption of "uniform" kinetics reduces the first-order differential equation describing the kinetics to a quasi-linear form, *the quasi-linearity does not carry over to second-order differential equations* such as those arising when diffusion is to be taken into account together with kinetics.

The notation which became standard is used here (Aris, 1991): x is the component label, and $G(x)$ is the dimensionless concentration distribution (normalized so that its zeroth and fist moments are unity) in the feed to a flow reactor with axial diffusion. With z the distance from the inlet divided by the reactor length, $g(x,z)$ is the dimensionless concentration distribution at position z; primes and double primes indicate partial differentiation with respect to z. We assume that the axial diffusivity is the same for all reactants, and we indicate with P the ratio of the diffusivity to the product of velocity and reactor length. Let $r(x,z)$ be the dimensionless rate of consumption of component x at position z, and let T be the dimensionless residence time in the reactor. The differential equation is an obvious extension of the classical one for a single component, and the boundary conditions are generalized versions of Danckwerts (1953):

$$Pg''(x,z) = g'(x,z) + Tr(x,z) \tag{1}$$

$$G(x) = g(x,0) - Pg'(x,0) \tag{2}$$

$$g'(x,1) = 0 \tag{3}$$

Before discussing in detail the nonlinear kinetic term $Tr(x,z)$, one can immediately identify the basic problem. Boundary conditions in Eqs. 2 and 3 are imposed at two different points ($z=0$ and $z=1$), and they have to be satisfied *for all values of x*: one has a two-point boundary value problem over an infinity of variables. This implies that any brute-force numerical attack on Eqs. 1-3 is bound to be very cumbersome,

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and a partly formal solution of the type discussed here is therefore useful.

We assume that the kinetics of the reactions are of the cooperative uniform type (Aris and Astarita, 1989a). Hence, the dimensionless reaction rate $r(x,z)$ is written as follows:

$$r(x,z) = xg(x,z)F[Q(z)] \tag{4}$$

where $F[\,]$ is the nonlinearity factor (Astarita and Ocone, 1988), the value of which is identically unity for first-order reactions. With triangular brackets identifying integration over the species spectrum, and u the component label when intended as a dummy variable, $Q(z)$ is a weighted concentration distribution spectrum at position z, $Q(z) = \langle K(u)g(u,z)\rangle$, where $K(u)$ is an appropriate kernel. The kinetics are cooperative, because the consumption rate of component x depends, through Q, on the whole local concentration distribution; they are uniform in that, since $K(u)$ depends on the dummy label u but not on the specific component x, $F[Q(z)]$ has, at any given position, the same value for all components. Catalytic reactions governed by Langmuir isotherm kinetics, where $F[Q] = 1/(1+Q)$, are an example of cooperative uniform kinetics (Astarita and Ocone, 1988).

Perturbation Expansion: CSTR Limit

The CSTR limit is obviously approached when the parameter P approaches infinity. We therefore proceed to a perturbation expansion where the perturbation parameter β is $1/P$. The perturbation is regular (Nayfeh, 1973). $g(x,z)$ and $Q(z)$ are written as:

$$g(x,z) = g_0(x,z) + \beta g_1(x,z) + \beta^2 g_2(x,z) + .\,. \tag{5}$$

$$Q(z) = Q_0(z) + \beta Q_1(z) + \beta^2 Q_2(z) + .\,. \tag{6}$$

$$Q_N(z) = \langle K(u)g_N(u,\,z)\rangle \tag{7}$$

The perturbation expansion can be carried out under the assumption that $F[\,]$ is differentiable as many times as one needs at all values that the base solution Q_0 may take. The structure of the problem is such that, at any given level of perturbation, the differential equation reduces to:

$$g_N''(x,z) = f_N(x,z) \tag{8}$$

where $f_N(x,z)$ is known from the solution of the lower-order problem. Hence, the nonlinearity of the kinetic term essentially disappears from the problem, except in so far as it determines the zero-order solution. At the zero-order level, one simply has $g_0''=0$. Now both boundary conditions are trivially satisfied by $g_0'=0$, and while this (correctly) tells us that g_0 does not depend on z, it does not tell us what the distribution $g_0(x)$ is. One now moves to the first-order level, and one obtains:

$$g_1'' = g_0' + xTg_0F(Q_0) \tag{9}$$

which, taking into account the exit boundary condition, integrates to:

$$g_1' = xTg_0F(Q_0)(z-1) \tag{10}$$

The inlet boundary condition is $G(x) = g_0(x) - g_1'(x,0)$, and hence:

$$G(x) = g_0(x) + xTg_0F(Q_0) \tag{11}$$

Equation 11 determines the value of $g_0(x)$, and it is the equation for the CSTR (Astarita and Nigam, 1989). One may now proceed to integrate Eq. 10 to obtain:

$$g_1 = xTg_0F(Q_0)(z^2/2 - z) + g_1(x,0) \tag{12}$$

and the "integration function" $g_1(x,0)$ is left to be determined by the second-order level of expansion. Proceeding to the second-order level, the algebra becomes rather nasty, but the procedure can be followed again to obtain $g_2'(x,z)$ in an explicit form which satisfies the exit boundary condition. The inlet boundary condition is now $g_2'(x,0) = g_1(x,0)$, so that the first-order solution is completed. However, again $g_2(x,z)$ is determined to within the "integration function" $g_2(x,0)$, which can be determined only from the third-order level of perturbation.

The concise discussion above shows that the regular perturbation expansion around the CSTR limit is relatively straightforward, but it does lead to a series of nested perturbation problems. For the case of a single reactant, a shortcut has been proposed in a different context (Astarita and Ocone, 1993b), but if this is applied to the case at hand to obtain a series of self-contained perturbation problems, one ends up with the need to solve an integral equation at every level of perturbation. With the procedure sketched above, the numerical effort is reduced to the solution of a series of ordinary linear nonhomogeneous differential equations which only contain definite integrals of known functions.

Perturbation Expansion: PFR Limit

In the PFR limit, the perturbation parameter is the inverse of the Peclet number, P. Since P multiplies the highest-order derivative (in addition to appearing in one of the boundary conditions), the perturbation expansion is seen to be a singular one (Nayfeh, 1973), and a boundary layer analysis will need to be developed; this is postponed to the next section.

The N-order term in the expansion of $xgF(Q)$ contains a leading term of the following form (all other terms are known from the lower-level solution):

$$g_NF(Q_0) + g_0F'(Q_0)Q_N \tag{13}$$

Q_N is a *linear* (integral) function of g_N, but it is not equal or proportional to it. The problem is easily seen at the first-order level:

$$g_1' + xTF(Q_0)g_1 = g_0'' - xTg_0F'(Q_0)Q_1 \tag{14}$$

$$g_1(x,0) = g_0'(x,0) \tag{15}$$

Equation 14, although linear, is an integro-differential equation for g_1. The approach which can be followed in its solution is sketched below. First, it is useful to define the following (known) functions:

$$M(z) = T\int_0^z F\,[Q_0(z')]dz' \tag{16}$$

$$N(x,z) = xTg_0(x,z)F'[Q_0(z)] \tag{17}$$

so that Eq. 14 reduces to:

$$g_1' + xM'(z)g_1 = g_0'' - N(x,z)Q_1(z) \tag{18}$$

The differential part can be solved to yield:

$$g_1(x,z) = \exp[-xM(z)][g_0'(x,0)$$

$$+ \int_0^z \exp[xM(z')][g_0''(x,z') - N(x,z')Q_1(z')]dz'] \tag{19}$$

Equation 19 is coupled with the definition of Q_1:

$$Q_1(z) = \langle K(u)g_1(u,z)\rangle \tag{20}$$

Substitution of Eq. 19 into Eq. 20 yields, after interchanging the order of integration:

$$Q_1(z) = A(z) - \int_0^z P(z,z')Q_1(z')dz' \tag{21}$$

where the (known) functions $A(z)$ and $P(z,z')$ are:

$$A(z) = \left\langle K(u)e^{uM(z)}\left[g_0'(u,0) + \int_0^z e^{uM(z')}g_0''(u,z')dz'\right]\right\rangle \tag{22}$$

$$P(z,z') = \langle K(u)e^{-u[M(z)-M(z')]}N(u,z')\rangle \tag{23}$$

Before discussing the solution of Eq. 21 it is useful to compare it with the CSTR integral equation for Q_0:

$$Q_0 = \langle K(u)G(u)/[1 + uTF(Q_0)]\rangle \tag{24}$$

Equation 24 is an integral equation for the scalar Q_0 [rather than for the function $Q_1(z)$ as is the case for Eq. 21]; however, Eq. 24 is nonlinear, while Eq. 21 is linear.

Equation 21 is a complete (nonhomogeneous: $A(z)$ is not identically zero) Volterra integral equation of the second kind (Guida, 1993; Petrovsky, 1971). Now suppose two distinct solutions of Eq. 21 exist. Their difference would be a nontrivial solution of the associated homogeneous Volterra equation, but the latter does not admit nontrivial solutions: the operator defined by the integral on the righthand side of Eq. 21 has a zero spectral radius (Kanwal, 1971); hence, the first alternative of the first Fredholm theorem holds and Eq. 21 admits a unique solution for the case at hand.

The solution is given by a method of successive approximations, where the Nth approximation to Q_1 is expressed directly in terms of the (N-1)th one:

$$Q_1^{(N)}(z) = A(z) - \int_0^z P(z,z')Q_1^{(N-1)}(z')dz' \tag{25}$$

$$Q_1^{(1)}(z) = A(z) \tag{26}$$

For any assigned $z = z^*$, let $P^*(z^*)$ be the maximum absolute value of $P(z^*,z')$ for z' between 0 and z^*, and let $A^*(z^*)$ be the maximum absolute value of $A(z)$ for z between 0 and z^*. Now it is easy to see that:

$$\mathrm{Max}\,|Q_1(z^*) - Q_1^{(1)}(z^*)| = P^*(z^*)A^*(z^*)z^* \tag{27}$$

$$\mathrm{Max}\,|Q_1(z^*) - Q_1^{(2)}(z^*)| = P^{*2}(z^*)A^*(z^*)z^{*2}/2 \tag{28}$$

$$\mathrm{Max}\,|Q_1(z^*) - Q_1^{(N)}(z^*)| = P^{*N}(z^*)A^*(z^*)z^{*N}/N! \tag{29}$$

Now let P^{**} [A^{**}] be the maximum value of $P^*(z^*)$ [$A^*(z^*)$] for z^* between 0 and 1. The righthand side of Eq. 29 cannot exceed $P^{**N}A^{**}/N!$, and hence the maximum possible residual when the approximation is truncated at the Nth iteration is established, and it is guaranteed to approach zero as the number of iterations increases.

Boundary Layer

The perturbation expansion discussed in the previous section is such that second-order differential equations are avoided, the nonlinearity persists only at the zero-order level, and the solution at any level has been obtained explicitly in terms of the solution at the next lower level. However, the compound solution found by truncating the procedure at some finite value of N does not satisfy boundary condition 3: the perturbation expansion only holds as an "outer" solution. Hence, a boundary layer develops near the reactor exit $z = 1$, and the "stretched coordinate" in the boundary layer is defined as:

$$y = (1 - z)/P \tag{30}$$

This reduces the differential equation in the boundary layer to (primes and double primes are now intended as derivative with respect to y):

$$g''(x,y) + g'(x,y) + PxTg(x,y)F\,[Q(y)] = 0 \tag{31}$$

This time the negligible (order P) term is the kinetic one, and therefore the boundary layer analysis is the same for any form of the kinetic function F [ ].

Because of boundary condition 3, Eq. 31 integrates the first time to:

$$g'(x,y) = Pf'(x,1)\exp(-y) \tag{32}$$

where f' is the derivative of the "outer" solution as obtained by truncating the expansion at some finite value of N. Equation 32 is subject to the classical boundary layer boundary condition that $g(x,y)$ approaches zero as y approaches infinity, and thus it integrates to the following form (where we have returned to the unstretched coordinate z):

$$g(x,z) = -Pf'(x,1)\exp[-(1-z)/P] \tag{33}$$

The inner solution in Eq. 33 always gives $g' = g/P$, and hence the sum of the inner and outer solutions satisfies both boundary conditions 2 and 3. Thus, a formal N-order solution has been found, which is constructed in N steps from the formal solution of the PFR problem.

Conclusions

Diffusion-convection-reaction problems in multicomponent mixtures lead, in the case of nonlinear kinetics, to differential equations where no warping of the independent variable z can make the problem a quasi-linear one. Direct numerical attack on such problems is very difficult because a two-point boundary value problem is imposed on an infinity of variables. However, perturbation expansions around the PFR and CSTR limits yield partly formal solutions, on the basis of which the numerical effort is reduced at worst to the evaluation of a finite series of definite integrals of known functions.

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