Simultaneous Autocatalytic Reaction and Diffusion in a Slab

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Autocatalytic reactions have not been studied in the context of the simultaneous reaction-diffusion problem. These reactions are found to possess all of the characteristics of nonautocatalytic irreversible and reversible reactions in addition to new and unusual behavior not available to such reactions. This is most apparent in the ratio of average reaction rate to surface reaction rate, or internal effectiveness factor, which becomes essentially unbounded in extreme cases. Necessary conditions for such behavior are developed here for bimolecular autocatalytic kinetics. An approximate first-order analog to autocatalytic behavior is presented.

The problem of simultaneous reaction and diffusion within porous media has received considerable attention (Aris, 1975). One major motivation is the analysis of heterogeneous catalytic kinetics in the presence of diffusion. The governing equations for certain types of biochemical behavior as well as for simultaneous diffusion with reactive absorption are also very similar to those traditionally studied in the context of catalysis. While heterogeneous catalysis is an important subset of all simultaneous reaction and diffusion problems, it is not the entire field. Homogeneous reactions that happen to occur within porous media are also included. The results discussed below apply to all known homogeneous bimolecular autocatalytic reactions occurring in porous media. In addition these results will apply to heterogeneous autocatalytic reactions that obey second-order kinetics. Important results for linear reaction/diffusion problems have appeared in numerous chemical engineering textbooks (such as Bird et al., 1960). Nonlinear problems in the field have typically displayed unusual behavior. The two most well publicized cases are for simultaneous diffusion with exothermic reaction and for simultaneous diffusion with a reaction exhibiting essentially inverse, or negative, order kinetics. Aris (1975) summarizes results for exothermic kinetics and negative power law kinetics. Morbidelli and Varma (1983) consider a Langmuir-Hinshelwood reaction that exhibits negative order behavior. The unusual behavior manifests in the internal effectiveness factor, or ratio of reaction rate averaged over the media to the reaction rate at the exposed external surface. In these cases the internal effectiveness factor can exceed unity for certain ranges of parameter values. The high internal effectiveness factors for exothermic reactions are caused by the rate of increase in the rate constant exceeding the rate of decrease in reactant species concentration. When reactions behave with essentially inverse order, the rate is observed to increase with decreasing reactant concentration. This occurs when a significant diffusion barrier limits reactant replenishment within the media.

Autocatalytic reactions, discussed below, are able to reach internal effectiveness factors that are also greater than unity. This behavior occurs in isothermal systems, where there is no enhancement of the rate constant. Furthermore, the internal effectiveness factor appears to be essentially unbounded with respect to the range of feasible parameters. Some of the highest internal effectiveness factors ever reported appear in this work. The source of this behavior is the sign change of the stoichiometric coefficient of the autocatalytic species, that is, a third mechanism for generating high internal effectiveness factors has been discovered. One possible reason that this aspect of simultaneous reaction and diffusion has been neglected is the lack of a reliable approximate linear analog. Two elementary reactions of second-order are considered here. One is the irreversible reaction $A + B \rightarrow 2A$. The other is the reversible reaction $A + B \rightleftarrows 2A$. These are less general than the corresponding Langmuir-Hinshelwood analogues, as well as less complicated to analyze. Results for second-order elementary reactions have generally been taken as lower bounds for equivalent Langmuir-Hinshelwood reactions in the context of the internal effectiveness factor.

Theory

The problem to be considered here is one of isothermal, steady-state reaction and diffusion in a slab which is sealed to mass transfer at one plane $x = 0$ and exposed to known species' concentrations at a second parallel plane $x = L$. The mass fluxes of the reacting species are taken as being proportional to the product of their constant effective diffusivities

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D_i times their concentration gradients. This leads to a coupled one-dimensional Dirichlet problem:

$$D_i \frac{d^2\hat{c}_i}{dx^2} = -\nu_i r \qquad i = A, B$$
$$\hat{c}_i = \hat{c}_{is} \qquad x = L$$
$$D_i \frac{d\hat{c}_i}{dx} = 0 \qquad x = 0 \tag{1}$$

where r is given by $k_f\hat{c}_A\hat{c}_B - k_r\hat{c}_A^2$. The reverse reaction rate constant is taken as zero in the case of the irreversible autocatalytic reaction. The stoichiometric coefficients ν_A and ν_B are plus one and minus one, respectively, for both the reversible and irreversible reaction cases. The two equation sets, Eq. 1, can be unified into a single set with the dimensionless concentration:

$$c = \frac{D_i(\hat{c}_i - \hat{c}_{is})}{\nu_i L^2 r_s} \tag{2}$$

where r_s is the reaction rate at the exposed slab surface $k_f\hat{c}_{As}\hat{c}_{Bs} - k_r\hat{c}_{As}^2$. This leads to the single ordinary differential equation with boundary conditions:

$$\frac{d^2c}{dz^2} = -\Phi_{2\text{nd}}c^2 + \Phi_{1\text{st}}^2 c - 1$$
$$c = 0 \qquad z = 1$$
$$\frac{dc}{dz} = 0 \qquad z = 0 \tag{3}$$

An analytical solution for this equation is available in Koopman and Lee (1992). The nature of the solution is controlled exclusively by the range of feasible values of the two parameters $\Phi_{2\text{nd}}$ and $\Phi_{1\text{st}}^2$. For irreversible second-order reactions, both parameters are non-negative and $\Phi_{2\text{nd}} \leq \Phi_{1\text{st}}^4/4$. For conventional reversible reactions, $\Phi_{2\text{nd}}$ retains the upper bound for irreversible reactions, but $\Phi_{2\text{nd}}$ is also able to take on negative values of arbitrary magnitude. The two parameters must be reexamined for the case of autocatalytic second-order irreversible and reversible reaction. First, define

$$\Phi_{A+B}^2 = \frac{k_f L^2 \hat{c}_{As}}{D_B} \qquad \Phi_{B+A}^2 = \frac{k_f L^2 \hat{c}_{Bs}}{D_A}$$
$$\Phi_{2A}^2 = \frac{k_r L^2 \hat{c}_{As}}{D_A} \tag{4}$$

These three quantities are known to be non-negative. Then the two moduli of Eq. 3 can be expanded in terms of the parameters of Eq. 4 as:

$$\Phi_{1\text{st}}^2 = (\Phi_{2A}^2 + \Phi_{A+B}^2) + (\Phi_{2A}^2 - \Phi_{B+A}^2)$$
$$\Phi_{2\text{nd}} = (\Phi_{2A}^2 + \Phi_{A+B}^2)(\Phi_{2A}^2 - \Phi_{B+A}^2) \tag{5}$$

where Φ_{2A}^2 is zero for the irreversible autocatalytic reaction case. It is apparent without further analysis that the situation for autocatalytic reactions will differ from that for conventional reactions. If the magnitude of Φ_{B+A}^2 is sufficiently large, then the first-order modulus $\Phi_{1\text{st}}^2$ will take on negative values. Restated in terms of the original physical constants, if

$$\hat{c}_{Bs} > \left(\frac{2k_r}{k_f} + \frac{D_A}{D_B}\right)\hat{c}_{As} \tag{6}$$

then this situation occurs. The choice of Φ^2 as the coefficient of the first power of concentration is a historical one that is rather unfortunate in the present context. It will be understood that $\Phi_{1\text{st}}^2$ is itself the first-order modulus, rather than its square root $\Phi_{1\text{st}}$ in what follows.

The problem of the feasible parameter space size is amenable to analysis through the methods of constrained optimization. The problem is stated: maximize $\Phi_{2\text{nd}}$, subject to constant $\Phi_{1\text{st}}^2$ and non-negative species moduli, Φ_{A+B}^2, Φ_{B+A}^2 and Φ_{2A}^2. The inequality constraints are not active when $\Phi_{1\text{st}}^2$ is positive, and the result obtained is $\Phi_{2\text{nd}} \leq \Phi_{1\text{st}}^4/4$. This is identical to the result for the upper bound on $\Phi_{2\text{nd}}$ for conventional second-order reactions (both irreversible and reversible). The inequality constraints are active when $\Phi_{1\text{st}}^2$ is negative, and the result obtained is $\Phi_{2\text{nd}} \leq 0$. The first-order modulus is unbounded in principle.

The macroscopic quantity of principle interest is the internal effectiveness factor. The result is obtained by taking a normalized integration of the rate expression over the medium and dividing it by the surface reaction rate. In terms of the dimensionless problem variables, it is given by:

$$\eta_{\text{int}} = \sqrt{2\Phi_{2\text{nd}}c(0)^3/3 - \Phi_{1\text{st}}^2 c(0)^2 + 2c(0)} \tag{7}$$

where $c(0)$ is the value of the dimensionless concentration at $z = 0$, the slab midplane. The midplane concentration can only be obtained by solving the differential equation, as in Koopman and Lee (1992). Results for positive $\Phi_{1\text{st}}^2$ are given in Koopman and Lee (1992) and are not reprinted here. It is useful to note that $c(0)$ is bounded between zero and the equilibrium states, or zeros, of the reaction-diffusion expression:

$$-\Phi_{2\text{nd}}c_{\text{eq}}^2 + \Phi_{1\text{st}}^2 c_{\text{eq}} - 1 = 0 \tag{8}$$

The behavior of the internal effectiveness factor for $\Phi_{1\text{st}}^2$ less than zero is shown in Figure 1. This is the quadrant of the feasible parameter space that contains the unusual behavior. Equation 6 gives the necessary condition to be in this quadrant. Large internal effectiveness factors are most easily obtained when the surface concentration of the autocatalytic species A is much smaller than that of the consumable reactant B. In practice, negative values of $\Phi_{1\text{st}}^2$ with extremely large magnitudes are difficult to obtain, especially when $\Phi_{2\text{nd}}$ is small in magnitude. This can be seen from Eq. 5, where $\Phi_{2\text{nd}}$ is the product of two quantities that add to give $\Phi_{1\text{st}}^2$.

When $\Phi_{B+A}^2 = \Phi_{2A}^2$, the first-order modulus $\Phi_{1\text{st}}^2$ is positive and $\Phi_{2\text{nd}}$ is zero. In this special case the autocatalytic

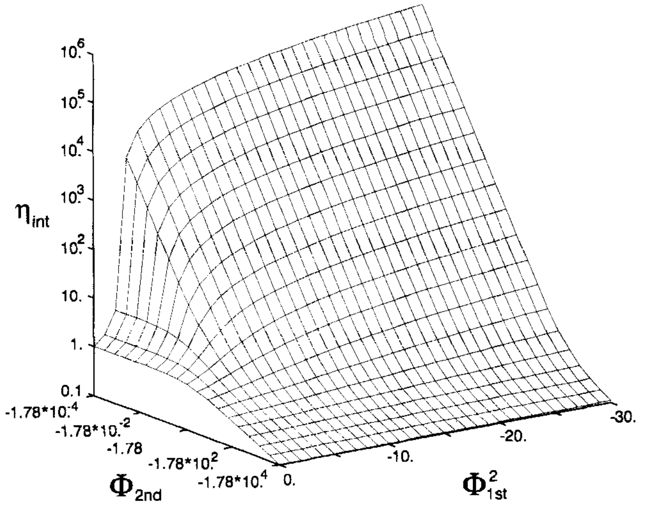

Figure 1. Internal effectiveness factor for second-order reaction and diffusion in a slab.

This quadrant of parameter space is restricted to elementary autocatalytic reactions. The range of Φ_{2nd}, -1.7778×10^{-4} to -1.7778×10^{4}, corresponds to a range of 0.1 to 10 in the generalized Thiele modulus as Φ^2_{1st} goes to zero.

reaction behaves exactly like a first-order conventional reaction with

$$\eta_{int} = \frac{\tanh(\Phi_{1st})}{\Phi_{1st}} \tag{9}$$

For $0 \geq \Phi^2_{1st} > -2.3$, the internal effectiveness factor approaches

$$\eta_{int} \rightarrow \frac{\tan\left(\sqrt{-\Phi^2_{1st}}\right)}{\sqrt{-\Phi^2_{1st}}} \tag{10}$$

very closely in the limit as Φ_{2nd} goes to zero. The expression in Eq. 10 goes to infinity at $\Phi^2_{1st} = -(\pi/2)^2$ and to unity as Φ^2_{1st} goes to zero. This result suggests that a limited first-order approximation to autocatalytic behavior could be obtained by using a negative rate constant in the first-order power law reaction problem originally studied by Thiele (1939). An equally valid interpretation is to change the sign of the stoichiometric coefficient in Eq. 1 rather than changing the sign of the rate constant. It has been common to omit the stoichiometric coefficient in the initial problem statement, but this oversight can easily be remedied in hindsight.

Conclusions

The analysis of simultaneous reaction and diffusion problems has been extended to the case of second-order autocatalytic elementary reaction and diffusion in a slab. An analytical solution exists for this problem. Second-order elementary autocatalytic reactions are found to possess the full range of behavior available to second-order reversible and irreversible conventional reactions. In addition, these autocatalytic reactions can access a region of parameter space not available to the conventional reactions. A simple necessary condition to access this quadrant is given in Eq. 6. This new parameter space region contains internal effectiveness factors greater than unity. The internal effectiveness factor becomes essentially unbounded in extreme cases. The sign of the stoichiometric coefficient of the autocatalytic species is responsible for the unusual behavior. This becomes the third known source of internal effectiveness factors larger than unity. The other two are exothermic reactions and virtual negative reaction orders. All three possess the feature that reaction rate can increase as the concentration of a reactant decreases. A limited first-order analog to autocatalytic behavior was also discovered as a result of this study. The problem of second-order autocatalytic reaction in a Langmuir-Hinshelwood rate form has three parameters after applying Eq. 2,

$$\frac{d^2c}{dz^2} = \frac{-\Phi_{2nd}c^2 + \Phi^2_{1st}c - 1}{(1+Kc)^q} \tag{11}$$

where q is either one or two, and K is the third parameter. The problem studied here is a special case of this problem when $K = 0$. General analytical solutions for Eq. 11 are not available, and do not appear possible in terms of elliptic functions of integrals.

Notation

c = dimensionless concentration given by Eq. 2
$\hat{c}$ = dimensional concentration
k = reaction rate constants
K = parameter in the Langmuir-Hinshelwood kinetic rate form
L = characteristic length of the slab (half-width)
r = kinetic rate expression
x = dimensional position variable
z = dimensionless position variable, x/L

Greek letters

η = effectiveness factor
ν = stoichiometric coefficient
Φ^2_{1st} = first-order or Thiele modulus
Φ_{2nd} = second-order modulus

Subscripts

A = specific chemical species
B = specific chemical species
eq = equilibrium value
f = forward direction
i = property appropriate to species, I
int = internal
r = reverse direction
s = at the exposed slab surface (at $x = L$)

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