Reaction Coordinates for Heterogeneous Flow Reactors: Physical Interpretation

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A number of chemical reaction engineering applications involve flow through porous media. Packed-bed reactors, chemical vapor deposition on porous substrates, and contaminant transport in groundwater are just three examples.

Analysis of these systems is complicated by the fact that local changes in reactants and products depend on both reaction rates and transport. Because of transport, the familiar concept of the extent of reaction along a reaction coordinate is less useful in the analysis of multiple heterogeneous reactions in a flow reactor. Extents of reaction are most useful for batch reactions and those reactors such as continuous stirred tanks for which extensions of the reaction coordinate concept can be made (Feinberg, 1987).

A relatively straightforward extension of the reaction coordinate idea is available for a class of models applicable for many practical heterogeneous flow problems as well (Friedly, 1991). Reaction coordinates can offer some advantages for computation, especially when treating problems having both equilibrium- and rate-controlled reactions (Friedly and Rubin 1992; Rubin, 1990). The purpose of this note is to offer a discussion of how trajectories in the subspace of these reaction coordinates can be used to gain a physical understanding of the progress of each reaction.

Model

Consider the problem of dispersed flow through a porous medium in which any number of homogeneous and heterogeneous reactions can take place. Mass balances at any position z and time t for all species in the mobile fluid phase are written (div = divergence operator; grad = gradient operator) as

$$\theta \frac{\partial C_i}{\partial t} = \mathrm{div}(D \,\mathrm{grad}\, C_i - vC_i) + \sum_{j=1}^{J} \nu_{ij} r_j, \quad i = 1, \cdots I \quad (1)$$

Similarly, the mass balances for surface, solid, or other immobile species are written

$$\rho \frac{\partial \bar{C}_i}{\partial t} = \sum_{j=1}^{J} \bar{\nu}_{ij} r_j, \quad i = 1, \cdots \bar{I} \quad (2)$$

The principal assumptions implicit in this set of model equations are that a continuum model is a reasonable approximation, the porosity θ and bulk density ρ are independent of time, and the dispersion coefficient D and Darcy velocity v are independent of both time and the concentrations. These assumptions are often used in several different types of applications, including packed-bed reactors.

Reaction Coordinates

Taking the approach suggested by the reaction coordinates for multiple reactions in a batch reactor, it is possible to separate the effects of local reactions from transport (Friedly, 1991). This is done by focusing on the stoichiometric subspace of the entire concentration space, but adding an effect of transport of the mobile species only. The transport contribution involves the stoichiometric subspace of the mobile species only. The following linear transformation of the vector of concentrations accomplishes this

$$X = \begin{pmatrix} \theta C_1 \\ \vdots \\ \theta C_I \\ \rho \bar{C}_1 \\ \vdots \\ \rho \bar{C}_{\bar{I}} \end{pmatrix} = S\xi + S^{\perp}\eta + \begin{pmatrix} s\xi_m + s^{\perp}\eta_m \\ 0 \end{pmatrix} \quad (3)$$

where $S = \begin{pmatrix} \nu \\ \bar{\nu} \end{pmatrix}$

is the matrix of stoichiometric coefficients of all reactions, which without loss of generality have been assumed linearly independent. $S^{\perp}$ is its orthogonal complement defined by $S^T S^{\perp} = 0$, which must exist if S has full rank. s is the set of all linearly independent columns of mobile species stoichiometric coefficient matrix ν and $s^{\perp}$ is its orthogonal comple-

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ment. Substituting Eq. 3 into the model Eqs. 1 and 2, it can be shown (Friedly, 1991) that the new dependent variable vectors ξ, η, ξ_m, and η_m satisfy

$$\frac{\partial \xi}{\partial t} = r \tag{4}$$

$$\frac{\partial \eta}{\partial t} = 0 \tag{5}$$

$$\frac{\partial \xi_m}{\partial t} = L(\xi_m + A\xi) \tag{6}$$

$$\frac{\partial \eta_m}{\partial t} = L\eta_m \tag{7}$$

Here, L is the transport operator $L\cdot = \operatorname{div}[D\operatorname{grad}(\cdot/\theta - v\cdot/\theta)]$ and A is the dependency matrix relating s to v, $v = As$.

Interpretation

Equations 4 and 5 are the familiar definitions of reaction coordinates or extents of reaction ξ and invariants η applicable for batch reactors. Each element ξ_j is associated with a single reaction rate r_j. The reaction rate r_j in general couples the corresponding ξ_j with the other ξ_k and with ξ_m and η_m. As seen in Eqs. 6 and 7, the vectors ξ_m and η_m arise solely because of the transport or flow. η_m is a reaction invariant, changing only because of flow and the boundary conditions on the problem. Each ξ_{m_j} can be associated with a single reaction, the one corresponding to the column of v used in s. ξ_{m_j} changes directly only because of the transport operator L in Eq. 6. It is independent of the local reaction rate, being coupled to reactions only through the transport of ξ in the term $LA\xi$.

For any reaction j having independent mobile phase stoichiometry, ξ_j and the corresponding ξ_{m_j} represent components of a two-dimensional reaction coordinate system. ξ_j may be considered the local reaction or batch contribution to the extent of reaction. ξ_{m_j} may be considered the flow contribution to the extent of reaction.

By following the time trajectory in the $\xi_j - \xi_{m_j}$ plane, it is possible to interpret the relative contributions of local reaction and transport at any point in the reactor. Just as the one-dimensional extent of reaction ξ_j measures the progress of the jth reaction in a complex batch reaction mixture, only the two-dimensional plane of $\xi_j - \xi_{m_j}$ is needed for complex reactions in a heterogeneous flow reactor (provided the model equations are reasonable). Since both Eqs. 4 and 6 are in the form of conservation equations, ξ_j and ξ_{m_j} can be interpreted physically as if they were conserved quantities. An increase in ξ_j at any time indicates reaction j is proceeding to the right at the local point in question. An increase in ξ_{m_j} indicates a net influx by transport of the conserved quantity ξ_{m_j}. It changes because of transport of both ξ_{m_j} itself and ξ_j, the direct result of local reaction in the adjacent locations.

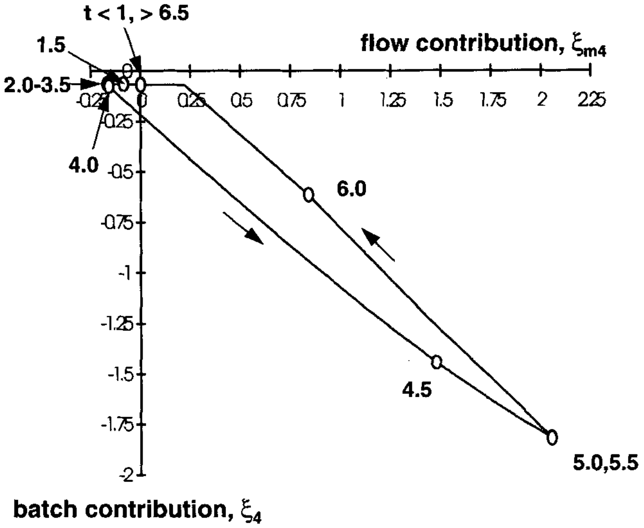

Figure 1. Reaction coordinate trajectory for reaction 4.

Example

The reaction sequence

$$\begin{array}{lll}
A_1 + A_3 \Leftrightarrow A_4 & K_1 = 1 & \text{homogeneous complexation} \\
A_1 + \bar{A}_4 \Leftrightarrow \bar{A}_1 & K_2 = 10 & \text{strong sorption} \\
A_2 + \bar{A}_4 \Leftrightarrow \bar{A}_2 & K_3 = 1 & \text{weak sorption} \\
\bar{A}_3 \Leftrightarrow A_2 + A_3 & K_4 = 1.2 & \text{dissolution/precipitation}
\end{array} \tag{8}$$

was used by Kirchner et al. (1984) to illustrate common interactions of species dissolved in groundwater with the sediment through which it flows. Simulations of the concentration histories have been performed for one-dimensional reactive transport using the parameter values suggested by Kirchner et al. (1984). The dimensionless value of $v = 1$ and $D = 40$ corresponds to a Peclet number of 1/40. Initially, the sediment was assumed to have a dimensionless sorbant $\bar{A}_4$ concentration of 5 and no solid A_3. The aqueous phase was assumed to contain only A_3 at a concentration of 1. At $z = 0$, the inlet concentration of the aqueous species A_1, A_2, and A_3 are increased to 1 at $t = 0$ and remain there. Results for the concentrations at position $z = 1$ downstream have been presented in Friedly and Rubin (1992) for several different combinations of rates of reaction and will not be repeated here. The reaction coordinate trajectories will be shown here for the case when all four reactions are in equilibrium.

Figure 1 shows the trajectory in the $\xi_4 - \xi_{m_4}$ reaction coordinate plane for the dissolution/precipitation reaction 4 at the position $z = 1$. The points are spaced at dimensionless time intervals of 0.5. The trajectory shows four rather distinct phases of the behavior. In the first phase between time about 1 and 2.5 ξ_{m_4} decreases from 0 while ξ_4 stays constant. This indicates that reaction products are being transported away from the point $z = 1$. However, no local reaction takes place. The right side of Eq. 6 is negative because transport removes some of the A_3 initially present. The right side of Eq. 4 is zero since there is initially no solid $\bar{A}_3$ present and the product concentrations are below the solubility product.

In the second phase from about $t = 3.8$ to 5, ξ_{m_4} reverses direction and ξ_4 decreases. This indicates that reaction 4 is proceeding to the left, precipitating $\bar{A}_3$. The aqueous products on the right side of reaction 4 have a net influx at $z = 1$, increasing ξ_{m_4}. At about $t = 5.7$ both ξ_{m_4} and ξ_4 reverse directions. Between about $t = 5.7$ and 6.1 the right sides of both Eqs. 4 and 6 are negative. This indicates that there is a net efflux of ξ_{m_4} and reaction products by transport, and the local reaction is proceeding to the right. The final segment from about $t = 6.1$ to 6.2 shows that again there is no reaction, because the solid $\bar{A}_3$ has been redissolved and again there is a net influx of products coming from the boundary conditions assumed for the problem.

Conclusions

This relatively simple example illustrates that it is possible to place a physical interpretation of what is happening locally in a heterogeneous flow reaction simply by looking at the trajectory in the $\xi_j - \xi_{m_j}$ plane. Regardless of how complicated the reaction mixture is and how many simultaneous reactions occur, the reaction coordinates are specific to individual reactions. There is a local or batch contribution to the extent of reaction ξ_j, which increases when the local reaction proceeds to the right and a flow contribution to the extent of reaction ξ_{m_j}, which increases when there is a net influx of either ξ_{m_j} or reaction products reflected in ξ_j being transported from elsewhere in the reactor. The transformations in Eq. 3 make this interpretation quite general for all heterogeneous reactors provided the transport is not significantly dependent on concentrations.

Notation

A_i, $\bar{A}_l$ = mobile aqueous species, surface or immobile species

C_i, $\bar{C}_i$ = mobile and immobile species concentrations

ν, $\bar{\nu}$, ν_{ij}, $\bar{\nu}_{ij}$ = stoichiometric coefficient matrices for mobile and immobile species, stoichiometric coefficients for mobile or immobile species i and reaction j

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