Extent of Reaction in Open Systems with Multiple Heterogeneous Reactions

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The familiar batch concept of extent of reaction is reexamined for systems of reactions occurring in open systems. Because species concentrations change as a result of transport processes as well as reactions in open systems, the extent of reaction has been less useful in practice in these applications. It is shown that by defining the extent of the equivalent batch reaction and a second contribution to the extent of reaction due to the transport processes, it is possible to treat the description of the dynamics of flow through porous media accompanied by many chemical reactions in a uniform, concise manner. This approach tends to isolate the reaction terms among themselves and away from the model partial differential equations, thereby enabling treatment of large problems involving both equilibrium and kinetically controlled reactions. Implications on the number of coupled partial differential equations necessary to be solved and on numerical algorithms for solving such problems are discussed. Examples provided illustrate the theory applied to solute transport in groundwater flow.

Introduction

Prigogine (Prigogine and Defay, 1954) may have been the first to point out the significance of what Everett has translated as the extent of reaction or reaction coordinate for a batch reaction. This well-known concept is now in common use in chemistry and chemical engineering (see for example Aris, 1969; Boudart, 1968; Froment and Bischoff, 1979). Aris (1963) pointed out the underlying basis in linear algebra for the utility of the reaction coordinate, and Aris and Mah (1963) defined the complement of the reaction coordinates as the reaction invariants. In a batch system involving *m*-independent reactions among *n* species, there will be *m* directions in the underlying *n* dimensional concentration vector space which correspond to each of the independent reactions. Concentration trajectories in the direction of any one of these reaction coordinates can be traced directly to the corresponding reaction. On the other hand, there will be *n*-*m* directions orthogonal to the reaction coordinates, in which there will be no motion at all due to the reactions.

In open systems, much of the advantage of defining extents of reaction and reaction invariants is lost. Concentrations change because of transport as well as reaction, and it is not always possible to separate out a contribution entirely due to each reaction from contributions that are reaction invariant. Diffusion rates in multicomponent systems differ somewhat for each species, and concentration changes due to reaction and diffusion are inextricably linked. On the other hand, Shapiro (1962) may have been the first to suggest using the extent of reaction in open systems when he considered homogeneous reactions in a transport field governed by a species-independent partial differential operator. Horn and Jackson (1972) (see also Feinberg, 1987) treated the open system of the stirred tank reactor by defining pseudoreactions to represent the net flow in and out.

There are broad classes of problems in which many chemical reactions occur in open systems. To select just one of many possible examples, the transport of solutes in groundwater supplies is currently of great importance because of concern over contamination. A foreign species such as a heavy metal ion may interact with the naturally occurring ions, chelating agents, and microbes occurring in the water as well as the many species occurring in or adsorbed on the minerals of the porous media through which the water flows. Sorting out which reactions and mass balances should be included in an analysis of this problem can be a formidable, yet important, task. Given the set of species and possible reactions along with the flow characteristics through the porous media, there is still considerable debate as to the best form of the mass balance equations to be used and their method of solution. For example, Yeh and Tripathi (1989) reviewed a number of approaches to formulating and solving the groundwater transport problem with equilibrium reactions and concluded that there are orders of magnitude differences in computational time depending on how the model is formulated. Rubin (1990) argues that computational efficiency can be increased by decreasing the number of coupled equations to be solved and shows, with broad classes of examples, that even using the most effective solution method the problem may differ substantially depending on the kinds of chemical equilibrium reactions present. Kirkner and Reeves (1988) and Rubin (1983) also pointed out how the mathematical problem is related to the chemistry. At the same time, there is growing concern that the traditional view of only equilibrium reactions in groundwater transport may be inadequate (see for example Wood et al., 1990; Bahr, 1990; Brusseau et al., 1990; Gopal and Friedly, 1989; Nicoud and Schweich, 1989; van der Zee et al., 1989). Models must include a spectrum of reactions, ranging from equilibrium-controlled to kinetically-controlled, with the possibility that the nature of any given reaction may change in the spatial domain of interest. It is well accepted (Plumb and Whitaker, 1988) that groundwater transport can be described in many situations by the convection-dispersion equations. Dispersion through porous media is largely a tortuous flow phenomenon and is usually independent of diffusion, making the partial-differential operator like that considered by Shapiro (1962).

The discussion above suggests that it would be of interest to have a general approach to formulating the model equations for open systems in which many rate processes having a wide variety of rates can be handled. The concept of an extent of reaction for each such reaction would be very attractive because it would tend to isolate one reaction from another and hopefully permit a more systematic treatment of problems of the type illustrated above. In the following sections, the theory for a broad class of problems including such systems will be developed based on the traditional ideas of extents of reaction. It will be shown that open systems governed by a species-independent operator may require the additional concept of a contribution to the extent of reaction due to the transport processes involved, which will be briefly called the flow extent. Reaction invariants will be defined for these problems as well. The implications of the resulting model equations then will be discussed in terms of their generality and limitations, their use with problems involving a wide range of rate constants, and their use in general purpose numerical solution codes. Examples taken from the groundwater transport literature will be used to illustrate the ideas.

Problem Formulation

Consider the possibility of m reactions occurring among $n+\bar{n}$ species in an open system. If some of the reactions are heterogeneous, it will be necessary to distinguish between species in the mobile fluid phase and the immobile phase. The bar over a symbol will always be used to designate the immobile phase. Therefore, the m reactions will involve n mobile-phase species and $\bar{n}$ immobile-phase species. These reactions will follow the general stoichiometry:

$$0 \Leftrightarrow \sum_{i=1}^{n} v_{ij} A_i + \sum_{i=1}^{\bar{n}} \bar{v}_{ij} \bar{A}_i, j = 1,m \tag{1}$$

where A represents the species and v represents the stoichiometric coefficients. Equation 1 applies to all m reactions that can be envisioned. They need not be reversible in general. By permitting the stoichiometric coefficients to be zero, it is possible to include homogeneous reactions in either phase. Each one of the reactions of Eq. 1 will have a rate of reaction r_j associated with it. The form of the rate of each reaction need not be specified further, but it will be assumed that each rate can be computed in terms of the concentrations of the species present. Similarly, it will be assumed that the equilibrium compositions of any equilibrium reaction can be computed by setting the rate to zero.

Consider these reactions occurring at a point in a continuum described by the usual mass balance equation (considered dimensionless) for species i in the mobile phase:

$$\theta \frac{\partial C_i}{\partial t} - LC_i = \sum_{j=1}^{m} v_{ij} r_j, i = 1,n \tag{2}$$

where θ represents the fraction of the volume at a "point" occupied by the mobile phase. The partial-differential operator L represents the net influx of the conserved species at the point. It may take the common form $L = -\nabla(V - D\nabla)$ for convection and dispersion through a porous medium. In what follows, it will be assumed that the operator L will be identical for all species as is often the case for transport through porous media. Similar to Eq. 2, the mass balance equation for species i in the immobile phase can be written:

$$\rho \frac{\partial \bar{C}_i}{\partial t} = \sum_{j=1}^{m} \bar{v}_{ij} r_j, i = 1,\bar{n} \tag{3}$$

where ρ represents the appropriate conversion factor for an immobile-phase concentration, based on solid mass or solid surface area, for example, to the point volume. The appropriate initial and boundary conditions will apply to Eqs. 2 and 3.

It is convenient to represent all of the quantities here in vector-matrix notation. Define the vector of concentrations in the mobile phase as $\underset{\sim}{C}$, the vector of concentrations in the immobile phase $\overline{\underset{\sim}{C}}$, the vector of reaction rates $\underset{\sim}{r}$ and the matrices of stoichiometric coefficients $\underset{\sim}{v}$ and $\overline{\underset{\sim}{v}}$:

$$\underset{\sim}{C} = \begin{bmatrix} C_1 \\ \vdots \\ C_n \end{bmatrix}, \ \overline{\underset{\sim}{C}} = \begin{bmatrix} \bar{C}_1 \\ \vdots \\ \bar{C}_{\bar{n}} \end{bmatrix}, \ \underset{\sim}{r} = \begin{bmatrix} r_1 \\ \vdots \\ r_m \end{bmatrix},$$

$$\underset{\sim}{v} = \begin{bmatrix} v_{11} & \dots & v_{1m} \\ \vdots & \vdots & \vdots \\ v_{n1} & \dots & v_{nm} \end{bmatrix}, \ \overline{\underset{\sim}{v}} = \begin{bmatrix} \bar{v}_{11} & \dots & \bar{v}_{1m} \\ \vdots & \vdots & \vdots \\ \bar{v}_{\bar{n}1} & \dots & \bar{v}_{\bar{n}m} \end{bmatrix} \tag{4}$$

Equations 2 and 3 can then be written in vector form:

$$\theta \frac{\partial \underset{\sim}{C}}{\partial t} - L\underset{\sim}{C} = \underset{\sim}{v}\,\underset{\sim}{r} \tag{5}$$

$$\rho\frac{\partial \overline{\underset{\sim}{C}}}{\partial t}=\overline{\underset{\sim}{\nu}}\,\underset{\sim}{r} \tag{6}$$

The initial and boundary conditions can also be written explicitly:

$$\text{at } t=0,\ \underset{\sim}{C}=\underset{\sim}{C}_0,\ \overline{\underset{\sim}{C}}=\overline{\underset{\sim}{C}}_0 \tag{7}$$

$$\text{at } \underset{\sim}{z}=0,\ \overline{\underset{\sim}{C}}=\overline{\underset{\sim}{C}}_{in} \text{ or } V\underset{\sim}{C}-D\nabla\underset{\sim}{C}=V\underset{\sim}{C}_{in} \tag{8}$$

$$\text{as } z\rightarrow\infty,\ \nabla\underset{\sim}{C}=0 \tag{9}$$

The boundary conditions here have been written for a one-dimensional, semiinfinite, spatial domain, but can easily be generalized to different parts of the boundary of the multidimensional medium.

The model (Eqs. 5 and 6) is broad enough to include a very large class of open systems in which heterogeneous reactions can occur. Although a single immobile phase is suggested, the model form is not at all restricted to one. Any number of solid phases and immobile fluid phases can also be accommodated by Eq. 6 by redefining concentrations in different immobile phases on the same basis. The important distinction between the phases is that the scalar operator L can be used to account for the influx at a point in the mobile phase and there is none in the immobile phase. In situations for which the commonly used approximation of film diffusion can be used (Villermaux, 1987), it can be treated as an effective reaction in this same model form.

Theory

Define the vector of concentrations of all species $\underset{\sim}{X}$ and the matrix of stoichiometric coefficients $\underset{\sim}{S}$:

$$\underset{\sim}{X}=\begin{bmatrix}\theta\underset{\sim}{C}\\ \hline \rho\overline{\underset{\sim}{C}}\end{bmatrix},\quad \underset{\sim}{S}=\begin{bmatrix}\underset{\sim}{\nu}\\ \hline \overline{\underset{\sim}{\nu}}\end{bmatrix} \tag{10}$$

It will be assumed that all of the reactions of Eq. 1 are linearly independent. Therefore, $\underset{\sim}{S}$ will have full rank and its columns can serve as basis vectors for the $n+\overline{n}$ dimensional composition space. $\underset{\sim}{S}$ and its orthogonal complement $\underset{\sim}{S}^{\perp}$ will completely span the composition space. In fact, for batch systems we know that the composition vector can be expanded in terms of the new basis $\underset{\sim}{X}=\underset{\sim}{S}\,\underset{\sim}{\xi}+\underset{\sim}{S}^{\perp}\,\underset{\sim}{\eta}$, where the components $\underset{\sim}{\xi}$ and $\underset{\sim}{\eta}$ are the extents of reaction and the reaction invariants (Feinberg, 1987). It will be convenient to develop the solution to Eqs. 5 and 6 in an analogous fashion for the open system, defining $\underset{\sim}{\xi}$ as the extent of reaction vector for the equivalent batch reactor.

Let the concentration vector be expanded partially in the form:

$$\underset{\sim}{X}=\underset{\sim}{S}\,\underset{\sim}{\xi}+\underset{\sim}{\Psi} \tag{11}$$

where the $\underset{\sim}{\xi}$ will be chosen to satisfy the equivalent batch relation:

$$\frac{\partial\underset{\sim}{\xi}}{\partial t}=\underset{\sim}{r} \tag{12}$$

and be called the extents of reaction (although to be more precise the term should be the extents of the equivalent batch reaction or batch contribution to the extents).

Because of the flow terms in Eq. 5, $\underset{\sim}{\Psi}$ will not lie totally in the orthogonal complement to the stoichiometric subspace. Instead, it too will in general have components in both the stoichiometric subspace and its complement. Introducing Eqs. 11 and 12 into Eqs. 5 and 6, we obtain:

$$\begin{aligned}\frac{\partial\underset{\sim}{\Psi}}{\partial t}&=L'\begin{bmatrix}\underset{\sim}{I} & 0\\ 0 & 0\end{bmatrix}(\underset{\sim}{S}\,\underset{\sim}{\xi}+\underset{\sim}{\Psi})\\ &=L'\begin{bmatrix}\underset{\sim}{\nu}\\ \hline 0\end{bmatrix}\underset{\sim}{\xi}+L'\begin{bmatrix}\underset{\sim}{I} & 0\\ \hline 0 & 0\end{bmatrix}\underset{\sim}{\Psi}\end{aligned} \tag{13}$$

where $L'=(1/\theta)L$. Clearly $\underset{\sim}{\Psi}$ is coupled to the extent of reaction vector. However, as should be expected, it is only coupled through the elements corresponding to the mobile-phase compositions. The elements corresponding to the immobile-phase components will indeed be invariant in time (and space) like the equivalent batch results. Therefore, if we write $\underset{\sim}{\Psi}$ as:

$$\underset{\sim}{\Psi}=\underset{\sim}{S}^{\perp}\,\underset{\sim}{\eta}+\begin{bmatrix}\underset{\sim}{\psi}\\ \hline 0\end{bmatrix} \tag{14}$$

the constant $\underset{\sim}{\eta}$ will satisfy the immobile-phase part of the problem completely and leave the $\underset{\sim}{\psi}$ term to satisfy the remainder of Eq. 13:

$$\frac{\partial\underset{\sim}{\psi}}{\partial t}=L'\,\underset{\sim}{\nu}\,\underset{\sim}{\xi}+L'\,\underset{\sim}{\psi} \tag{15}$$

Equation 15 can be handled in much the same way as the original Eqs. 5 and 6 by focusing on the underlying n-dimensional, mobile-phase concentration vector space. It is convenient to define the mobile-phase stoichiometric subspace in terms of the linearly-independent columns of the mobile-phase stoichiometric coefficients $\underset{\sim}{\nu}$. Although it has been assumed that all reactions are independent and $\underset{\sim}{S}$ has full rank, this does not imply that $\underset{\sim}{\nu}$ has full rank. Take all of the linearly-independent columns of $\underset{\sim}{\nu}$ to form the basis of the stoichiometric subspace for the mobile phase $\underset{\sim}{s}$. Because $\underset{\sim}{s}$ contains the set of linearly-independent columns of $\underset{\sim}{\nu}$, the remaining columns can always be written as a linear combination of the $\underset{\sim}{s}$. Therefore, $\underset{\sim}{\nu}$ can always be written in factored form:

$$\underset{\sim}{\nu}=\underset{\sim}{s}\,\underset{\sim}{A} \tag{16}$$

The dependency matrix $\underset{\sim}{A}$ will have a single unity in columns corresponding to the columns of $\underset{\sim}{\nu}$ included in $\underset{\sim}{s}$ but in general full columns of coefficients for the linearly-dependent columns of $\underset{\sim}{\nu}$. Using Eq. 16 in Eq. 15, it is possible to write the solution for $\underset{\sim}{\psi}$ in the form:

$$\boldsymbol{\psi} = \boldsymbol{s}\,\boldsymbol{\xi}_m + \boldsymbol{s}^{\perp}\,\boldsymbol{\eta}_m \tag{17}$$

where $\boldsymbol{s}^{\perp}$ is the orthogonal complement of the mobile-phase stoichiometric subspace $\boldsymbol{s}$. The components $\boldsymbol{\eta}_m$ are true reaction invariants (although not generally invariant in time and space) satisfying

$$\frac{\partial \boldsymbol{\eta}_m}{\partial t} = L'\,\boldsymbol{\eta}_m \tag{18}$$

The components $\boldsymbol{\xi}_m$ will satisfy

$$\frac{\partial \boldsymbol{\xi}_m}{\partial t} = L'\,\boldsymbol{\xi}_m + L'\,\boldsymbol{A}\,\boldsymbol{\xi} \tag{19}$$

The components $\boldsymbol{\xi}_m$ couple the contribution of the transport operator in the open system to the extents of the equivalent batch reaction. They will be called the flow extents for short.

Specification of the appropriate initial and boundary conditions will completely define the problem equivalent to Eqs. 5 through 9. Since $\boldsymbol{S}$ and $\boldsymbol{S}^{\perp}$ completely span the concentration space, the initial conditions (Eqs. 7) can be satisfied with the extent of reaction $\boldsymbol{\xi}$ and the invariant $\boldsymbol{\eta}$:

$$\begin{bmatrix} \theta \boldsymbol{C}_0 \\ \rho \boldsymbol{\overline{C}}_0 \end{bmatrix} = \boldsymbol{X}_0 = \boldsymbol{S}\,\boldsymbol{\xi}_0 + \boldsymbol{S}^{\perp}\,\boldsymbol{\eta}_0 \tag{20}$$

permitting the additional mobile-phase contributions to be zero:

$$\boldsymbol{\xi}_{m_0} = 0, \quad \boldsymbol{\eta}_{m_0} = 0 \tag{21}$$

Similarly, the mobile-phase concentration values on the boundaries can be expanded in terms of the $\boldsymbol{s}$ and $\boldsymbol{s}^{\perp}$ basis vectors:

$$\theta \boldsymbol{C}_{in} - \boldsymbol{\nu}\,\boldsymbol{\xi} - (\boldsymbol{S}^{\perp}\,\boldsymbol{\eta}_0)_m = \boldsymbol{s}\,\boldsymbol{\xi}_{m_{in}} + \boldsymbol{s}^{\perp}\,\boldsymbol{\eta}_{m_{in}} \tag{22}$$

where $(\cdot)_m$ refers to just first n mobile-phase components of the vector. Therefore, both $\boldsymbol{\xi}_m$ and $\boldsymbol{\eta}_m$ will satisfy boundary conditions of the form of Eqs. 8 and 9.

In summary, the vector of concentrations can be written in the form:

$$\begin{bmatrix} \theta \boldsymbol{C} \\ \rho \boldsymbol{\overline{C}} \end{bmatrix} = \boldsymbol{X} = \boldsymbol{S}\,\boldsymbol{\xi} + \boldsymbol{S}^{\perp}\,\boldsymbol{\eta}_0 + \begin{bmatrix} \boldsymbol{s}\,\boldsymbol{\xi}_m + \boldsymbol{s}^{\perp}\,\boldsymbol{\eta}_m \\ 0 \end{bmatrix}$$

$$= \begin{bmatrix} \boldsymbol{s}\,(\boldsymbol{A}\,\boldsymbol{\xi} + \boldsymbol{\xi}_m) \\ \boldsymbol{\overline{\nu}}\,\boldsymbol{\xi} \end{bmatrix} + \boldsymbol{S}^{\perp}\,\boldsymbol{\eta}_0 + \begin{bmatrix} \boldsymbol{s}^{\perp}\,\boldsymbol{\eta}_m \\ 0 \end{bmatrix} \tag{23}$$

The extent of reaction $\boldsymbol{\xi}$ will satisfy Eq. 12 along with initial condition of Eq. 20. The flow extent $\boldsymbol{\xi}_m$ will satisfy Eq. 19 along with zero initial conditions and boundary conditions of the form of Eqs. 8 and 9 with Eq. 22. Actually, the combination

$$\boldsymbol{\zeta} = \boldsymbol{\xi}_m + \boldsymbol{A}\,\boldsymbol{\xi} \tag{24}$$

always appears together in both Eqs. 19 and 23 and will satisfy the boundary conditions as a group. The invariant $\boldsymbol{\eta}$ will satisfy the initial condition of Eq. 20. The reaction invariant $\boldsymbol{\eta}_m$ will satisfy Eq. 18 along with zero initial conditions and boundary conditions of the form of Eqs. 8 and 9 with Eq. 22.

Discussion

The form of the solution shown in Eq. 23 is instructive. The middle equality shows that the solution for the state vector is made up of two parts. The first part represents the contributions of the equivalent batch reactions. It is conveniently presented in terms of components with respect to a basis of the stoichiometric subspace and its orthogonal complement. The extent of reaction vector, satisfying the same Eq. 12 as is expected in a batch problem, contains the components in the stoichiometric subspace. As in a batch problem, the true invariant components $\boldsymbol{\eta}_0$ appear as well.

In an open system, there is an additional contribution of the transport operator. That contribution only directly affects the concentrations of the species in the mobile phase that are being transported. Indirectly, these compositions will affect the extent of reaction $\boldsymbol{\xi}$, however, because they will in general appear in the rate expressions in Eq. 12. The contribution of the transport operator, unlike the equivalent batch contribution, directly influences just the mobile-phase compositions. Therefore, it is not convenient to represent its effect in terms of the complete stoichiometric subspace. Instead, the mobile-phase stoichiometric subspace and its complement are appropriate. The components of response in the mobile-phase stoichiometric subspace $\boldsymbol{\xi}_m$ represent the contribution of transport to the extent of reaction or flow extent for short. The flow and batch contributions to the extent of reaction are coupled directly in the partial differential equation (Eq. 19). In general, Eqs. 12 and 19 must be solved together. Because of this, the solution for the extent of reaction, although it satisfies Eq. 12 which appears exactly like the batch reactor equation, will reflect the presence of the flow extent as well. Finally, the reaction invariant components $\boldsymbol{\eta}_m$ are indeed completely independent of the reaction rates, but may vary with time and spatial position satisfying Eq. 18.

The last equality of Eq. 23 groups the solution parts together as reaction-dependent and reaction-independent. The first part includes the extent of reaction and flow. The last two terms include the invariant and reaction invariant terms. It is clear from this form that there is no convenient subspace in the $n + \overline{n}$ dimensional concentration space that will contain the reaction-dependent parts of a trajectory. Instead, it appears that the most convenient way of looking at the response is in the form of the middle equality, with the sum of two contributions: one of the complete stoichiometric subspace and the other of the mobile phase stoichiometric subspace. The latter in general neither is a subspace of the former nor intersects with it only at the origin.

It is interesting to compare the approach used here with similar approaches used previously for open systems. If the reactions involve only mobile-phase species, the subspaces spanned by $\boldsymbol{S}$ and $\boldsymbol{s}$ coincide. Then, Shapiro (1962) suggested that use of the extent of reaction is valid because there is no distinction between $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_m$. Horn and Jackson (1972) and subsequently Feinberg (1987) treated complex reaction networks in continuous stirred-tank reactors, described by the operator $LC_i = (1/\tau)(C_{i_{in}} - C_i)$, instead of a partial differential operator in Eq. 2. In contrast to the approach developed above, Horn and Jackson defined pseudoreactions to account for the flow in and out of the reactor. They effectively cast Eqs. 5 and 6 into the form

$$\frac{\partial \underset{\sim}{X}}{\partial t} = \begin{bmatrix} \underset{\sim}{I} & \underset{\sim}{v} \\ 0 & \overline{\underset{\sim}{v}} \end{bmatrix} \begin{bmatrix} L' \underset{\sim}{C} \\ \underset{\sim}{r} \end{bmatrix}$$

and used the augmented stoichiometric subspace

$$\underset{\sim}{S}_{aug} = \begin{bmatrix} \underset{\sim}{I} & \underset{\sim}{v} \\ 0 & \overline{\underset{\sim}{v}} \end{bmatrix}$$

and its complement as the convenient basis in which to express the solution. The augmented extent of reaction vector resulting from this approach $\underset{\sim}{\xi}^T_{aug} = [\,\underset{\sim}{\xi}_{flow} \;\; \underset{\sim}{\xi}\,]$ includes the same extent of reaction defined above but also a flow extent that incorporates not only the flow extent $\underset{\sim}{\xi}_m$ defined above but also the reaction invariants $\underset{\sim}{\eta}_m$ and even parts of the invariant term $\underset{\sim}{S}^{\perp}\,\underset{\sim}{\eta}_0$. For the partial differential equation models of interest here, it appears that it is more useful to identify specifically all variables that are truly reaction invariants and provide the equations they satisfy.

The above derivations have cast the mass balance equations for a broad class of transport problems with multiple reactions in a heterogeneous medium into a rather general and concise form. First, there will be $n + \overline{n} - \text{rank}(\underset{\sim}{S})$ invariants $\underset{\sim}{\eta}_0$ which can be obtained simply from the initial conditions. The equations to be solved then will always consist of $n - \text{rank}(\underset{\sim}{s})$ reaction-invariant, partial-differential equations (Eq. 18). If the transport operator L is linear as is common for dispersed flow through a saturated porous medium, these equations are uncoupled from each other and can be solved independent of all of the rest. Then, there are $\text{rank}(\underset{\sim}{s})$ linear, scalar, partial-differential equations for the flow extents (Eq. 19). These too are uncoupled in the sense of each component being directly independent of the others. However, since Eq. 24 linearly relates the flow extent vector with the extent of reaction vector, the components of Eq. 19 remain indirectly coupled. In general, Eq. 19 will have to be solved along with the $m = \text{rank}(\underset{\sim}{S})$ nonlinear, ordinary-differential equations for the extent vector (Eq. 12). Two things have been accomplished by the transformations. The total number of partial differential equations to be solved is no different, but those in Eqs. 18 and 19 are linear and in one sense uncoupled. The m nonlinear, ordinary-differential equations may in fact be greater in number than the $\overline{n}$ in the original Eq. 3. However, what has been accomplished is the isolation of each reaction into Eq. 12 and away from the partial-differential equations.

The latter accomplishment permits a relatively straightforward switch from kinetically-controlled reactions considered up to this point to equilibrium-controlled reactions. If all of the reactions are in equilibrium, the only difference is that the extents of reaction $\underset{\sim}{\xi}$ need to be solved from the equilibrium relation $\underset{\sim}{r} = 0$, instead of from Eq. 12. These algebraic equations need to be solved simultaneously with the flow extents in Eq. 19. A solution algorithm for algebraic equilibrium equations may well be simplified by having a single variable ξ_i which will always appear in the corresponding reaction equilibrium $r_i = 0$ (even though it still may be coupled with the entire extent vector). This should eliminate the need to treat different classes of equilibrium reactions differently (Rubin, 1990). Furthermore, this formulation of the transport problem rather easily permits the use of kinetic expressions for some reactions and equilibrium expressions for others, even in different regions of the spatial domain. All that is necessary is to compute the extent of reaction ξ_i for each reaction from either the kinetic expression (Eq. 12) or from the algebraic equilibrium expression.

Such a general approach to reacting transport problems has implications for writing general simulation codes. Yeh and Tripathi (1989) discussed the advantages of numerical approaches that tend to keep the partial-differential transport equations separated as much as possible from the algebraic chemical equilibria. Furthermore, these approaches tend to be more readily adaptable to kinetically controlled reactions. Rubin (1980) emphasized the importance of decoupling the partial-differential equations from each other as well as from the equilibrium reactions. The approach developed in this article would appear to include the best features of both Yeh and Tripathi's conclusions and Rubin's work.

Applications

The above theory will be illustrated using two examples taken from the literature on solute transport in groundwater. The first involving only a single reaction will be used to illustrate the ideas in their simplest form, while the second will be used to show how they apply to many reactions.

Surface exchange reaction

Suppose the simple exchange reaction:

$$A_1 + \overline{A_2S} \Leftrightarrow A_2 + \overline{A_1S}$$

takes place as the fluid flows through a one-dimensional, semiinfinite, porous exchange medium (Persaud and Wierenga, 1982). In this case, the model of Eqs. 5 and 6 applies with

$$\underset{\sim}{v} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} = \underset{\sim}{s}$$

and

$$\overline{\underset{\sim}{v}} = \begin{bmatrix} 1 \\ -1 \end{bmatrix}.$$

Therefore, the solution Eq. 23 will take the form:

$$\begin{bmatrix} \theta \underset{\sim}{C} \\ \rho \overline{\underset{\sim}{C}} \end{bmatrix} = \begin{bmatrix} -1 \\ 1 \\ 1 \\ -1 \end{bmatrix} \xi + \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & -1 \\ 0 & 1 & 0 \end{bmatrix} \underset{\sim}{\eta}_0 + \begin{bmatrix} \begin{bmatrix} -1 \\ 1 \end{bmatrix} \xi_m + \begin{bmatrix} 1 \\ 1 \end{bmatrix} \eta_m \\ \begin{bmatrix} 0 \\ 0 \end{bmatrix} \end{bmatrix}$$

Any other linear combination of the columns of $\underset{\sim}{S}^{\perp}$ would suffice as well. Here, there are three scalar functions that satisfy Eqs. 12, 19 and 18. The linear equation for η_m can be solved independent of the reaction. The linear partial-differential equation for the flow extent ξ_m is indirectly coupled to the nonlinear reaction rate through the extent of reaction ξ.

Persaud and Wierenga's (1982) results suggested that the reaction could be considered in local equilibrium. If the rate expression $r = k[C_1\bar{C}_{2S} - (C_2\bar{C}_{1S})/K]$ is assumed, the equilibrium-controlled reaction can easily be treated by replacing Eq. 12 by $r = 0$. Using the above expressions for the concentrations, the extent of reaction ξ can be solved at every time and position from

$$0 = [-(\xi + \xi_m) + \eta_{1_0} + \eta_m][-\xi + \eta_{2_0}] - \frac{[(\xi + \xi_m) + \eta_{1_0} + \eta_{3_0} + \eta_m][\xi + \eta_{2_0} - \eta_{3_0}]}{K}$$

instead of from Eq. 12.

High-order reaction network

Rubin (1990) systematically developed the governing mass balance equations in a form convenient for numerical computation for the broad classes of groundwater transport problems with networks of equilibrium reactions. The application of the theory developed above to the most complicated example worked out by Rubin will be outlined. Consider the reactions among four primary cations and four anions in solution. Three surface exchange reactions,

$$A_1 + \overline{A_3S} \Leftrightarrow A_3 + \overline{A_1S},\ A_1 + \overline{A_5S} \Leftrightarrow A_5 + \overline{A_1S},$$
$$A_1 + \overline{A_7S} \Leftrightarrow A_7 + \overline{A_1S},$$

three classical dissolution-precipitation reactions,

$$\overline{A}_{12} \Leftrightarrow A_1 + A_2,\ \overline{A}_{14} \Leftrightarrow A_1 + A_4,\ \overline{A}_{32} \Leftrightarrow A_3 + A_2,$$

and eight homogeneous complexation reactions,

$$A_1 + A_6 \Leftrightarrow A_{16},\ A_1 + A_8 \Leftrightarrow A_{18},\ A_3 + A_6 \Leftrightarrow A_{36},\ A_3 + A_8 \Leftrightarrow A_{38},$$
$$A_5 + A_2 \Leftrightarrow A_{52},\ A_5 + A_4 \Leftrightarrow A_{54},\ A_7 + A_2 \Leftrightarrow A_{72},\ A_7 + A_4 \Leftrightarrow A_{74},$$

involve 16 mobile-phase species and seven immobile species.

These 14 reactions have a stoichiometric coefficient matrix $\underset{\sim}{S}$ which is 23×14. The reactions have been selected to be independent so that rank $(\underset{\sim}{S}) = 14$. Therefore there will be 14 extents of reaction $\underset{\sim}{\xi}$ to be determined by Eq. 12 or equivalent equilibrium relations. The orthogonal complement matrix $\underset{\sim}{S}^{\perp}$ will be of dimension 23×9. Therefore, there will be nine invariants $\underset{\sim}{\eta}$ determined from the initial conditions. The 16×14 matrix of mobile-phase stoichiometric coefficients $\underset{\sim}{v}$ only has a rank of 13, however. Note for example that the mobile-phase concentrations in the first exchange reaction appear with the same stoichiometric coefficients as they do in the difference of the third and the first dissolution reactions. This causes $\underset{\sim}{v}$ to have less than full rank. The choice of mobile-phase stoichiometric subspace consisting of only the last 13 columns of $\underset{\sim}{v}$ leads to the 13×14 $\underset{\sim}{A}$ dependency matrix of Eq. 16 displayed with $\underset{\sim}{v}$:

$$\underset{\sim}{v} = \begin{bmatrix}
-1 & -1 & -1 & 1 & 1 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix},$$

$$\underset{\sim}{A} = \begin{bmatrix} \begin{bmatrix} 0 \\ 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} & \underset{\sim}{I} \end{bmatrix},\ \underset{\sim}{S}^{\perp} = \begin{bmatrix}
1 & 0 & 0 \\
-1 & 0 & 0 \\
1 & 0 & 0 \\
-1 & 0 & 0 \\
1 & 0 & 0 \\
-1 & 1 & 0 \\
1 & 0 & 0 \\
-1 & 0 & 1 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}$$

The first column of $\underset{\sim}{A}$ represents the dependent first reaction (column) in $\underset{\sim}{v}$. The 13×13 identity matrix in $\underset{\sim}{A}$ represents all of the remaining linearly independent columns of $\underset{\sim}{v}$. It is easy to verify that each of the columns of $\underset{\sim}{S}^{\perp}$ shown above is orthogonal to each column of $\underset{\sim}{v}$ and consequently $\underset{\sim}{S}$ as well.

The complete problem to be solved will consist of three reaction invariants $\underset{\sim}{\eta}_m$ of the form of Eq. 18 which can be solved independent of the rest. Then, there will be 13 flow extents $\underset{\sim}{\xi}_m$ satisfying the linear Eq. 19, which are in one sense all uncoupled from each other too. However, they are indirectly coupled through the 14 algebraic equations $\underset{\sim}{r} = 0$ when the reactions are in equilibrium. These results, which of course agree with Rubin's conclusion, can be determined immediately by defining the dimensions of the problem's stoichiometric subspace and the mobile-phase stoichiometric subspace and their complements in the formulation presented here. In contrast to Rubin's (1990) result, however, this approach avoids the direct substitution of equilibrium relations into partial-differential equations. A particular advantage of this approach is that by isolating the reactions each reaction may be separately considered either equilibrium- or kinetically-controlled, and each can be treated in a similar manner, independent of whether it is a homogeneous, surface exchange, or precipitation reaction.

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Literature Cited

Aris, R., *Elementary Chemical Reactor Analysis*, Prentice-Hall, Englewood Cliffs, NJ (1969).

Aris, R., "The Fundamental Arbitrariness in Stoichiometry," *Chem. Eng. Sci.*, **18**, 554 (1963).

Aris, R., and R. H. S. Mah, "Independence of Chemical Reactions," *Ind. Eng. Chem. Fundam.*, **2**, 90 (1963).

Bahr, J. M., "Kinetically Influenced Terms for Solute Transport Affected by Heterogeneous and Homogeneous Classical Reactions," *Water Resour. Res.*, **26**, 21 (1990).

Boudart, M., *Kinetics of Chemical Processes*, Prentice-Hall, Englewood Cliffs, NJ (1968).

Brusseau, M. L., R. E. Jessup, and P. S. C. Rao, "Modeling the Transport of Solutes Influenced by Multiprocess Nonequilibrium," *Water Resour. Res.*, **25**, 1971 (1989).

Feinberg, M., "Chemical Reaction Network Structure and the Stability of Complex Isothermal Reactors: I. The Deficiency Zero and Deficiency One Theorems," *Chem. Eng. Sci.*, **42**, 2229 (1987).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, Wiley, New York (1979).

Gopal, R., and J. C. Friedly, "Analysis of Transport of Sparingly Soluble Solutes in Groundwater," *Encyclopedia of Environmental Control Technology*, Vol. 3, Ch. 17, p. 487, Wastewater Treatment Technology, P. N. Cheremisinoff, ed., Gulf Publishing, Houston (1989).

Horn, F., and R. Jackson, "General Mass Action Kinetics," *Arch. Rational Mech. Anal.*, **47**, 81 (1972).

Kirkner, D. J., and H. Reeves, "Multicomponent Mass Transport with Homogeneous and Heterogeneous Chemical Reactions: Effect of the Chemistry on the Choice of Numerical Algorithm: 1. Theory," *Water Resour. Res.*, **24**, 1719 (1988).

Nicoud, R. M., and D. Schweich, "Solute Transport in Porous Media with Solid-Liquid Mass Transfer Limitations: Application to Ion Exchange," *Water Resour. Res.*, **25**, 1071 (1989).

Plumb, O. A., and S. Whitaker, "Dispersion in Heterogeneous Porous Media: 1. Local Volume Averaging and Large-Scale Averaging; 2. Predictions for Stratified and Two Dimensional Spatially Periodic Systems," *Water Resour. Res.*, **24**, 913, 927 (1988).

Prigogine, I., and R. Defay, *Chemical Thermodynamics*, Eng. trans. by D. H. Everett, Longmans Green & Co., London (1954).

Rubin, J., "Solute Transport with Multisegment, Equilibrium-Controlled Reactions: a Feedforward Simulation Method," *Water Resour. Res.*, **26**, 2029 (1990).

Rubin, J., "Transport of Reacting Solutes in Porous Media: Relation between Mathematical Nature of Problem Formulation and Chemical Nature of Reactions," *Water Resour. Res.*, **19**, 1231 (1983).

Shapiro, N., "Chemical Reaction Occurring with Migration," *Proc. Symp. Appl. Math*, **14**, 83 (1962).

van der Zee, S., F. Lens, and M. Lauer, "Prediction of Phosphate Transport in Small Columns with an Approximate Sorption Kinetics Model," *Water Resour. Res.*, **25**, 1353 (1989).

Villermaux, J., "Chemical Engineering Approach to Dynamic Modeling of Linear Chromatography: a Flexible Method for Representing Complex Phenomena from Simple Concepts," *J. Chromatogr*, **406**, 11 (1987).

Wood, W. W., T. F. Kraemer, and P. P. Hearn, "Intragranular Diffusion: an Important Mechanism Influencing Solute Transport in Clastic Aquifers?" *Sci.*, **247**, 1569 (1990).

Yeh, G. T., and V. S. Tripathi, "A Critical Evaluation of Recent Developments in Hydrogeochemical Transport Models of Reactive Multichemical Components," *Water Resour. Res.*, **25**, 93 (1989).

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