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Abstract

A wide range of numerical methods are available to integrate coupled differential equations of first-order decay networks. When greatly differing decay rates exist in a reaction network, the stiffness of ordinary differential equations arises and requires additional effort to obtain solutions numerically. Although analytical solutions are preferred, they are limited to relatively simple reaction networks and a small number of species. In this paper, we propose a methodology to formulate analytical solutions of ODEs for a unlimited number of species and more generalized reaction networks, including multi-daughter branching and multi-parent converging reactions. The solution scheme can be further applied to obtain analytical solutions of transport systems coupled by complex decay networks.

Keywords Reactive transport · Decay · Ingrowth · First-order reaction · Decomposition

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Nomenclature

a	Concentration in transformed domain (ML^{-3})
$\mathbf{A}$	First-order reaction matrix (T^{-1})
$b_{i,j}$	Number of branches between species i and j
c	Concentration (ML^{-3})
c^o	Initial or boundary concentration (ML^{-3})
$\mathbf{c}$	Vector of concentrations (ML^{-3})
$\mathbf{c}^o$	Vector of initial or boundary concentrations (ML^{-3})
D	Dispersion coefficient ($\mathrm{L}^2\mathrm{T}^{-1}$)
f	Analytical solution of a single-species transport (-)
i	Species index (-)
j	Species index (-)
k	First-order decay rate (T^{-1})
K_d	Partitioning coefficient ($\mathrm{L}^3\mathrm{M}^{-1}$)
m	Species index of a species' ancestor (-)
M	Total number of species (-)
$n_{i,j}$	Number of generations between species i and j (-)
n_p	Number of parent species (-)
R	Retardation factor (-)
s	Solid-phase concentration (MM^{-1})
$\mathbf{S}$	Transformation matrix (-)
$\mathbf{S}^-$	Inverse transformation matrix (-)
t	Time (T)
$t_{1/2}$	Half-life time (T)
v	Flow velocity (LT^{-1})
x	Distance (L)

Greek Symbols

α	Branching factor (-)
β	Branching factor (-)
β_i	Intermediate parameter of solution (Bear, 1979)
ζ	Branching index (-)
$\mathbf{\Lambda}$	Diagonal matrix containing all decay rates (T^{-1})
ϕ	Porosity (-)
ρ_b	Bulk density (ML^{-3})

1. Introduction

Modeling of reactive transport coupled with complex decay networks is computationally expensive, even impossible, when the number of species is large or stiff reactions are involved. Operator-splitting is a practical approach to simulate transport system coupled with reactions (Valocchi and Malmstead, 1992; Lu et al., 1996; Barry et al., 1996; 2000). To overcome the stiffness of reactions and to enhance computational efficiency, Geiser (2001) first coupled a closed-form solution (Sun et al., 1999) of a first-order decay chain with the numerical solution of transport in his operator-splitting scheme. However, the OS procedure of Geiser (2001) is limited to a typical case of a sequential and unimolecular reaction chain. Therefore, there is a need to investigate a generalized closed-form solution approach for a wide range of decay networks.

A generic decay network is composed of M different species. All decay reactions are assumed to be first order. The reactants and products of a reaction are referred to as *parent* and *daughter* species. The reaction network with a single parent and a single daughter is called as *sequential-reaction network* (Bateman, 1910; Sun et al., 1999). The reaction network with multiple parents and a single daughter is called as a *multi-parent converging network*. The reaction network with one parent and multiple daughter species is called as a *multi-daughter branching network*. The branching factor is defined as the proportional productivity for a specific daughter from a given parent.

In the absence of spatial dependence, the ordinary differential equations of sequential first-order reactions are usually solved numerically by using ODE solvers (Clement et al., 1998; Clement, 2001; Yamamoto et al., 2007). To get a numerically accurate solution, the ODE system is expected to be well-conditioned. Often, when first-order reaction rates of neighboring species span many orders of magnitude, the decay system may become stiff and require small time steps to meet the convergence standard (Thomas and Barber, 1994).

The solution of a decay network can be symbolically described using the matrix-exponential format (Moler and van Loan, 1978; Thomas and Barber, 1994; Yamamoto et al., 2007). There are various approaches to compute the matrix exponential of decay equations. Those approaches include the fourth-order Runge-Kutta-Gill method (Radhakrishnan and Hindmarsh, 1993), the Padé approximant and the Taylor-series expansion of matrix exponential (Thomas and Barber, 1994), the Bateman analytical solution (Bateman, 1910), and the matrix decomposition method (Pressyanov, 2002; Lu et al., 2003). Compared to numerical solutions, analytical solutions of first-order decay networks provide an accurate and reliable prediction. However, the Bateman (1910) analytical solution is limited to the sequential first-order reaction system.

Laplace transforms are often used for solving differential equations (Bateman, 1910; Pressyanov, 2002). However, the Laplace approach relies on infinite integrals. When the number of species is large or a branching network is involved, the inverse Laplace transforms, if possible, become inconvenient. In fact, the original Bateman equations can be solved using matrix mathematics (Moral and Pacheco, 2003; Lu et al., 2003; Sun et al., 2004; Yuan and Kernan, 2007). As anticipated by Moral and Pacheco (2003), the algebraic approach can be extended to solve branching reaction networks.

In order to achieve the computational efficiency and accuracy, we propose a generalized approach of the analytical matrix decomposition for a wide range of decay networks. The objective of this paper is to describe and demonstrate the decomposition method for analytical solution development of decay networks in batch reactors. Then, the analytical solutions are coupled with transport models using analytical formulation and operator-splitting methods. The methodology is applicable to transport coupled by radionuclide decay, biodegradation of chlorinated solvents, denitrification, etc.

2. Model Development

The mass balance equations of a first-order decay network can be expressed compactly using matrices as

$$\frac{d\mathbf{c}}{dt} = \mathbf{A}\ \mathbf{c} \tag{1}$$

where $\mathbf{c}$ is the vector of species concentrations and $\mathbf{A}$ is the first-order reaction matrix defined by the reaction network architecture and decay rates. The solution of Eq. (1) can be symbolically expressed as

$$\mathbf{c} = \exp\left[\mathbf{A}t\right]\mathbf{c}^{o} \tag{2}$$

where $\mathbf{c}^{o}$ is the vector of initial concentrations. The calculation of the concentration vector mainly relies on the evaluation of the exponential matrix.

The singular-value decomposition of a first-order reaction matrix establishes the relationship between the coupled-reaction system in the real-world system and its independent system in the transformed domain (Clement, 2001; Lu et al., 2003). Instead of using numerical methods, we prefer to develop an analytical formulation system, described in this section for the singular-value decomposition. The transformation matrices are formulated based on the reaction network architecture.

2.1. Sequential Reaction Network

In order to illustrate the generalized transformation, we start with the sequential-reaction network (Bateman, 1910; Sun et al., 1999; Clement, 2001; Bear and Cheng, 2010, p.∼480). The sequential-reaction network is also called as a dominant-daughter reaction chain and has been extensively studied. Both analytical and numerical solutions of the reaction chain are available in the literature and can be used for comparison purposes. As shown in Figure 1, every daughter product has only one parent and every parent has only one dominant daughter product.

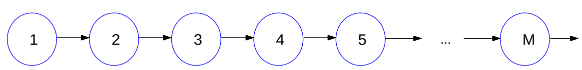

Figure 1. Sequential-reaction network of TCE degradation. Every daughter species except the very first ancestor has only one parent species and every parent species except the end product has only one daughter species.

Then, the first-order reaction matrix, $\mathbf{A}$, is expressed as

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & \cdots & 0 \\ k_1 & -k_2 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & k_{i-1} & -k_i \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & k_{M-1} & -k_M \end{bmatrix}. \tag{3}$$

Equation (1) can be solved analytically (Sun et al., 1999) and numerically (Clement et al., 1998). The focus of this paper is to generalize the solution scheme of analytical solutions for various reaction networks. The hypothesis for this approach is that the reaction matrix $\mathbf{A}$ can be analytically described as

$$\mathbf{A} = \mathbf{S}\boldsymbol{\Lambda}\mathbf{S}^{-}, \tag{4}$$

where $\boldsymbol{\Lambda}$ is an $M \times M$ diagonal matrix containing the eigenvalues of $\mathbf{A}$, $\mathbf{S}$ is a matrix whose columns are linearly independent eigenvectors of $\mathbf{A}$, $\mathbf{S}^{-}$ is the inverse matrix of $\mathbf{S}$, and the diagonal components of $\boldsymbol{\Lambda}$ are the exact decay rates of the species. We expect a closed-form expression for $\mathbf{S}$ and $\mathbf{S}^{-}$.

Substituting Eq. (4) into Eq. (1) and multiplying by $\mathbf{S}^-$, Eq. (1) becomes

$$\frac{d\mathbf{a}}{dt} = \mathbf{\Lambda a}, \qquad \mathbf{a} = \mathbf{S}^-\mathbf{c}. \tag{5}$$

Each ODE in Eq. (5) is independent of other ODEs and has exactly the same format as the standard exponential function as its closed-form solution (Sun et al., 2008).

$\mathbf{S}^-$ and $\mathbf{S}$ are called transformation matrices between the concentration domain and the transformed domain and are expressed analytically as finite products of fractions of the form

$$S^-_{i,j} = \prod_{l=1}^{n_{i,j}} \frac{k_{m(l)}}{k_{m(l)} - k_i} \tag{6}$$

$$S_{i,j} = \frac{k_j}{k_i - k_j} \prod_{l=1}^{n_{i,j}-1} \frac{k_{m(l)}}{k_{m(l)} - k_j} \tag{7}$$

where i is the current species index and j is an ancestor of species i, $m(l)$ is the species index of lth ancestor of i, and $n_{i,j}$ is the generation number from species j to i. If j is not an ancestor of i, $S^-_{i,j}$ and $S_{i,j}$ are defined as zero. $S^-_{i,j} = S_{i,j} = 1$ when $i = j$.

The component $S^-_{i,j}$ is interpreted as the inheritance of species i from its ancestors from j to $i-1$. For example, for $i = 5$ and $j = 1$ in the five-species sequential chain, where $m(l) = l$ and $n_{5,1} = 4$,

$$S^-_{5,1} = \prod_{l=1}^{4} \frac{k_l}{k_l - k_5} = \underbrace{\frac{k_1}{k_1 - k_5}}_{1\to5} \cdot \underbrace{\frac{k_2}{k_2 - k_5}}_{2\to5} \cdot \underbrace{\frac{k_3}{k_3 - k_5}}_{3\to5} \cdot \underbrace{\frac{k_4}{k_4 - k_5}}_{4\to5}. \tag{8}$$

Equation (8) shows four fractions of the sequential inheritance from species 1 to 5. Figure 2 shows the formulation concept of $S^-_{5,1}$ and $S_{5,1}$.

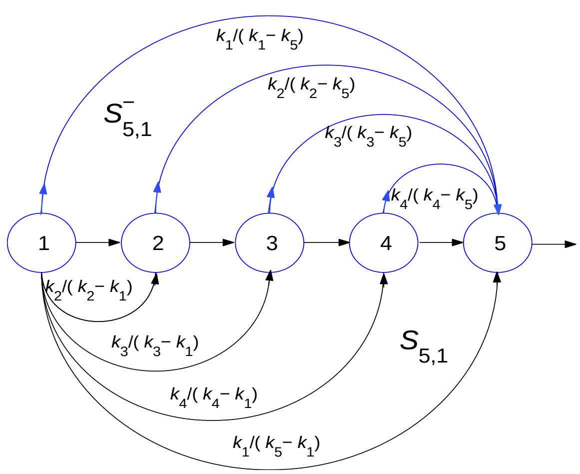

Figure 2. Graphic interpretation of $S^-_{5,1}$ and $S_{5,1}$.

The component $S_{i,j}$ is interpreted as how much of the descendants (between j and i) of species j inherit from j. For example, for $i = 5$ and $j = 1$

$$S_{5,1} = \frac{k_1}{k_5 - k_1} \prod_{2}^{4} \frac{k_l}{k_l - k_1} = \underbrace{\frac{k_1}{k_5 - k_1}}_{1 \Rightarrow 5} \cdot \underbrace{\frac{k_2}{k_2 - k_1}}_{1 \rightarrow 2} \cdot \underbrace{\frac{k_3}{k_3 - k_1}}_{1 \rightarrow 3} \cdot \underbrace{\frac{k_4}{k_4 - k_1}}_{1 \rightarrow 4} . \tag{9}$$

The first fatcor takes a different format from the rest and describes the direct relation between species 1 and 5 as indicated by $\Rightarrow$. Then, $\mathbf{S}^-$ and $\mathbf{S}$ for the five-species sequential reaction chain can be explicitly expressed

$$\mathbf{S}^- = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_1-k_2} & 1 & 0 & 0 & 0 \\ \frac{k_1}{k_1-k_3} \cdot \frac{k_2}{k_2-k_3} & \frac{k_2}{k_2-k_3} & 1 & 0 & 0 \\ \frac{k_1}{k_1-k_4} \cdot \frac{k_2}{k_2-k_4} \cdot \frac{k_3}{k_3-k_4} & \frac{k_2}{k_2-k_4} \cdot \frac{k_3}{k_3-k_4} & \frac{k_3}{k_3-k_4} & 1 & 0 \\ \frac{k_1}{k_1-k_5} \cdot \frac{k_2}{k_2-k_5} \cdot \frac{k_3}{k_3-k_5} \cdot \frac{k_4}{k_4-k_5} & \frac{k_2}{k_2-k_5} \cdot \frac{k_3}{k_3-k_5} \cdot \frac{k_4}{k_4-k_5} & \frac{k_3}{k_3-k_5} \cdot \frac{k_4}{k_4-k_5} & \frac{k_4}{k_4-k_5} & 1 \end{bmatrix} \tag{10}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_2-k_1} & 1 & 0 & 0 & 0 \\ \frac{k_1}{k_3-k_1} \cdot \frac{k_2}{k_2-k_1} & \frac{k_2}{k_3-k_2} & 1 & 0 & 0 \\ \frac{k_1}{k_4-k_1} \cdot \frac{k_2}{k_2-k_1} \cdot \frac{k_3}{k_3-k_1} & \frac{k_2}{k_4-k2} \cdot \frac{k_3}{k_3-k_2} & \frac{k_3}{k_4-k_3} & 1 & 0 \\ \frac{k_1}{k_5-k_1} \cdot \frac{k_2}{k_2-k_1} \cdot \frac{k_3}{k_3-k_1} \cdot \frac{k_4}{k_4-k_1} & \frac{k_2}{k_5-k_2} \cdot \frac{k_3}{k_3-k_2} \cdot \frac{k_4}{k_4-k_2} & \frac{k_3}{k_5-k_3} \cdot \frac{k_4}{k_4-k_3} & \frac{k_4}{k_5-k_4} & 1 \end{bmatrix} . \tag{11}$$

The transformation matrices $\mathbf{S}$ and $\mathbf{S}^-$ derived here for the sequential first-order decay chain are, respectively, identical to $\mathbf{S}$ and $\mathbf{T}$ matrices of Moral and Pacheco (2003). Eq. (6) itself is equivalent to the transformation of Sun et al. (1999) from the coupled concentration domain to the independent one. For the inverse transform from "a" to "c", Sun et al. (1999) used the sequential substitution based on Eq. (6). For this reason, the closed-form solution of Sun et al. (1999) in the real concentration domain is limited to simple sequential or non-converging reaction networks. In order to facilitate the formulation of more generalized decay networks with a unlimited number of species, both $\mathbf{S}$ and $\mathbf{S}^-$ are formulated. Note that a slight format difference is necessary before the product sign in Eq. (7).

2.2. Multi-parent Converging Network

If multiple species decay to produce the same daughter product, the reaction network is called a multi-parent converging network. Compared to the sequential-reaction chain, the ordinary differential equation of the converging daughter product is coupled by more than one parent concentrations. This issue has been discussed in the literature since Bateman (1910). Recently, numerical decomposition (Clement, 2001) and case-specific analytical decomposition (Lu et al., 2003; Sun et al., 2004) have been used to solve those converging networks.

An example of a converging-reaction network is illustrated in Figure 3 (Peterson et al., 2007) and expressed as

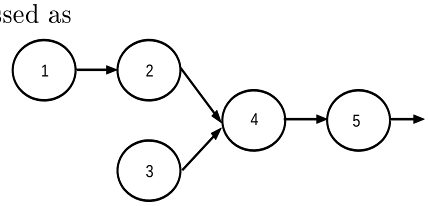

Figure 3. A converging decay network (Peterson et al., 2007).

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 & 0 \\ 0 & 0 & -k_3 & 0 & 0 \\ 0 & k_2 & k_3 & -k_4 & 0 \\ 0 & 0 & 0 & k_4 & -k_5 \end{bmatrix}. \tag{12}$$

Species 2 and 3 decay to produce the same species 4. Using Eqs. (6) and (7), the reaction matrix (12) of the coupled converging reactions can be decomposed as $\mathbf{A} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-}$, where $\mathbf{\Lambda}$ is a diagonal matrix with exactly the same components as in matrix A.

$$\mathbf{S}^{-} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_1-k_2} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{k_1}{k_1-k_4}\cdot\frac{k_2}{k_2-k_4} & \frac{k_2}{k_2-k_4} & \frac{k_3}{k_3-k_4} & 1 & 0 \\ \frac{k_1}{k_1-k_5}\cdot\frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_3}{k_3-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_4}{k_4-k_5} & 1 \end{bmatrix} \tag{13}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_2-k_1} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{k_1}{k_4-k_1}\cdot\frac{k_2}{k_2-k_1} & \frac{k_2}{k_4-k_2} & \frac{k_3}{k_4-k_3} & 1 & 0 \\ \frac{k_1}{k_5-k_1}\cdot\frac{k_2}{k_2-k_1}\cdot\frac{k_4}{k_4-k_1} & \frac{k_2}{k_5-k_2}\cdot\frac{k_4}{k_4-k_2} & \frac{k_3}{k_5-k_3}\cdot\frac{k_4}{k_4-k_3} & \frac{k_4}{k_5-k_4} & 1 \end{bmatrix}. \tag{14}$$

2.3. Multi-daughter Branching Network

In addition to the sequential and converging reaction patterns, we now consider the multi-daughter branching reaction nature in this subsection. As shown in Figure 4, Lu et al. (2003) provides a simple TCE degradation with sequential, converging, and branching features. A parent species may decay to produce multiple daughter products.

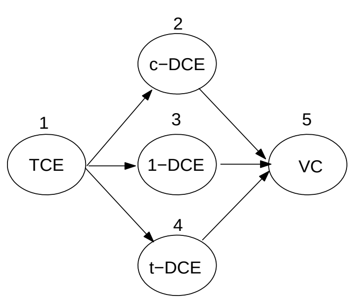

Figure 4. TCE decay series (Lu et al., 2003). TCE=trichloroethylene, c-DCE=cis-dichloroethylene, t-DCE = trans-dichloroethylene, 1-DCE = 1,1-dichloroethylene, VC = vinyl chloride.

The branching factors from species 1 to species 2, 3, 4 are expressed using α_1, α_2, and α_3 with $\alpha_1 + \alpha_2 + \alpha_3 = 1$. Three branches are involved in the relation between species 1 and 5. Therefore, the basic forms of $\mathbf{S}^{-}$ (Eq. 6) and $\mathbf{S}$ (Eq. 7), are modified as

$$S^{-}_{i,j} = \sum_{\zeta=1}^{b_{i,j}} \left[\alpha_\zeta \prod_{l=1}^{n_{i,j}} \frac{k_{m(l)}}{k_{m(l)} - k_i} \right] \tag{15}$$

$$S_{i,j} = \sum_{\zeta=1}^{b_{i,j}} \left[\alpha_\zeta \frac{k_j}{k_i - k_j} \prod_{l=1}^{n_{i,j}-1} \frac{k_{m(l)}}{k_{m(l)} - k_j} \right] \tag{16}$$

where ζ is the branch number index and $b_{i,j}$ is the number of branches to connect species i and j.

The reaction matrix of TCE degradation is written (Lu et al., 2003) as

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 \\ \alpha_1 k_1 & -k_2 & 0 & 0 & 0 \\ \alpha_2 k_1 & 0 & -k_3 & 0 & 0 \\ \alpha_3 k_1 & 0 & 0 & -k_4 & 0 \\ 0 & k_2 & k_3 & k_4 & -k_5 \end{bmatrix}. \tag{17}$$

Taking $S^-_{5,1}$ as an example, the generation number between species 1 and 5, $n_{1,5}$, is 2 and branching number, $b_{1,5}$, is 3.

$$S^-_{5,1} = \overbrace{\alpha_1 \frac{k_1}{\underbrace{k_1 - k_5}_{1\to 5}} \cdot \frac{k_2}{\underbrace{k_2 - k_5}_{2\to 5}}}^{\zeta=1} + \overbrace{\alpha_2 \frac{k_1}{\underbrace{k_1 - k_5}_{1\to 5}} \cdot \frac{k_3}{\underbrace{k_3 - k_5}_{3\to 5}}}^{\zeta=2} + \overbrace{\alpha_3 \frac{k_1}{\underbrace{k_1 - k_5}_{1\to 5}} \cdot \frac{k_4}{\underbrace{k_4 - k_5}_{4\to 5}}}^{\zeta=3} \tag{18}$$

$$S_{5,1} = \overbrace{\alpha_1 \frac{k_1}{\underbrace{k_5 - k_1}_{1\Rightarrow 5}} \cdot \frac{k_2}{\underbrace{k_2 - k_1}_{1\to 2}}}^{\zeta=1} + \overbrace{\alpha_2 \frac{k_1}{\underbrace{k_5 - k_1}_{1\Rightarrow 5}} \cdot \frac{k_3}{\underbrace{k_3 - k_1}_{1\to 3}}}^{\zeta=2} + \overbrace{\alpha_3 \frac{k_1}{\underbrace{k_5 - k_1}_{1\Rightarrow 5}} \cdot \frac{k_4}{\underbrace{k_4 - k_1}_{1\to 4}}}^{\zeta=3}. \tag{19}$$

The transformation matrices derived using Eqs. (15) and (16) are identical to $\mathbf{S}^-$ and $\mathbf{S}$ matrices of Lu et al. (2003),

$$\mathbf{S}^- = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{\alpha_1 k_1}{k_1 - k_2} & 1 & 0 & 0 & 0 \\ \frac{\alpha_2 k_1}{k_1 - k_3} & 0 & 1 & 0 & 0 \\ \frac{\alpha_3 k_1}{k_1 - k_4} & 0 & 0 & 1 & 0 \\ \frac{k_1}{k_1 - k_5}\left(\frac{\alpha_1 k_2}{k_2 - k_5} + \frac{\alpha_2 k_3}{k_3 - k_5} + \frac{\alpha_3 k_4}{k_4 - k_5}\right) & \frac{k_2}{k_2 - k_5} & \frac{k_3}{k_3 - k_5} & \frac{k_4}{k_4 - k_5} & 1 \end{bmatrix} \tag{20}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{\alpha_1 k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 \\ \frac{\alpha_2 k_1}{k_3 - k_1} & 0 & 1 & 0 & 0 \\ \frac{\alpha_3 k_1}{k_4 - k_1} & 0 & 0 & 1 & 0 \\ \frac{k_1}{k_5 - k_1}\left(\frac{\alpha_1 k_2}{k_2 - k_1} + \frac{\alpha_2 k_3}{k_3 - k_1} + \frac{\alpha_3 k_4}{k_4 - k_1}\right) & \frac{k_2}{k_5 - k_2} & \frac{k_3}{k_5 - k_3} & \frac{k_4}{k_5 - k_4} & 1 \end{bmatrix}. \tag{21}$$

2.4. Retardation Consideration

Ordinary differential equations of a first-order decay network can be explicitly expressed as

$$\frac{dc_i}{dt} = \sum_{j=1}^{n_p} k_j c_j - k_i c_i, \quad \forall i = 1, \cdots, M \tag{22}$$

$$\frac{ds_i}{dt} = \sum_{j=1}^{n_p} k_j s_j - k_i s_i, \quad \forall i = 1, \cdots, M \tag{23}$$

where c_i [ML^{-3}] and s_i [MM^{-1}] are liquid and solid concentrations of species i, and n_p is the number of parents of i. If $n_p = 1$ for all species except the very first ancestor, Eq. (22) alone is the Bateman model (1910).

The concentration of the adsorbed species is often expressed as a linear function of its liquid-phase concentration

$$s_i = K_d^i c_i, \quad \forall i = 1, 2, \cdots, M \tag{24}$$

where K_d^i is the partitioning coefficient. Therefore, the derivative of the solid-phase concentration (23) can be described as

$$\frac{\rho_b}{\phi}\frac{ds_i}{dt} = \sum_{j=1}^{n_p} \frac{\rho_b K_d^j}{\phi} k_j c_j - \frac{\rho_b K_d^i}{\phi} k_i c_i. \tag{25}$$

Combining (22) and (25),

$$R_i \frac{dc_i}{dt} = \sum_{j=1}^{n_p} R_j k_j c_j - R_i k_i c_i, \quad \forall i = 1, \cdots, M \tag{26}$$

where $R_i = 1 + \rho_b K_d^i/\phi$. Then,

$$\frac{dc_i}{dt} = \sum_{j=1}^{n_p} \frac{R_j}{R_i} k_j c_j - k_i c_i, \quad \forall i = 1, \cdots, M \tag{27}$$

Equation (27) is different from the standard ODEs solved by Bateman (1910). The ratio of retardation factors of a parent species to its daughter contributes to the concentration prediction of the daughter species. Correspondingly, the transformation matrices are modified as

$$S_{i,j}^- = \frac{R_j}{R_i} \sum_{\zeta=1}^{b_{i,j}} \left[\alpha_\zeta \prod_{l=1}^{n_{i,j}} \frac{k_{m(l)}}{k_{m(l)} - k_i} \right] \tag{28}$$

$$S_{i,j} = \frac{R_j}{R_i} \sum_{\zeta=1}^{b_{i,j}} \left[\alpha_\zeta \frac{k_j}{k_i - k_j} \prod_{l=1}^{n_{i,j}-1} \frac{k_{m(l)}}{k_{m(l)} - k_j} \right] \tag{29}$$

Taking the converging network in Figure 3 as an example, the reaction matrix, $\mathbf{S}^-$, and $\mathbf{S}$ matrices are

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 \\ \frac{R_1}{R_2}k_1 & -k_2 & 0 & 0 & 0 \\ 0 & 0 & -k_3 & 0 & 0 \\ 0 & \frac{R_2}{R_4}k_2 & \frac{R_3}{R_4}k_3 & -k_4 & 0 \\ 0 & 0 & 0 & \frac{R_3}{R_5}k_4 & -k_5 \end{bmatrix} \tag{30}$$

$$\mathbf{S}^{-} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{R_1}{R_2}\cdot\frac{k_1}{k_1-k_2} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{R_1}{R_4}\cdot\frac{k_1}{k_1-k_4}\cdot\frac{k_2}{k_2-k_4} & \frac{R_2}{R_4}\cdot\frac{k_2}{k_2-k_4} & \frac{R_3}{R_4}\cdot\frac{k_3}{k_3-k_4} & 1 & 0 \\ \frac{R_1}{R_5}\cdot\frac{k_1}{k_1-k_5}\cdot\frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{R_2}{R_5}\cdot\frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{R_3}{R_5}\cdot\frac{k_3}{k_3-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{R_4}{R_5}\cdot\frac{k_4}{k_4-k_5} & 1 \end{bmatrix} \tag{31}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{R_1}{R_2}\cdot\frac{k_1}{k_2-k_1} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{R_1}{R_4}\cdot\frac{k_1}{k_4-k_1}\cdot\frac{k_2}{k_2-k_1} & \frac{R_2}{R_4}\cdot\frac{k_2}{k_4-k_2} & \frac{R_3}{R_4}\cdot\frac{k_3}{k_4-k_3} & 1 & 0 \\ \frac{R_1}{R_5}\cdot\frac{k_1}{k_5-k_1}\cdot\frac{k_2}{k_2-k_1}\cdot\frac{k_4}{k_4-k_1} & \frac{R_2}{R_5}\cdot\frac{k_2}{k_5-k_2}\cdot\frac{k_4}{k_4-k_2} & \frac{R_3}{R_5}\cdot\frac{k_3}{k_5-k_3}\cdot\frac{k_4}{k_4-k_3} & \frac{R_4}{R_5}\cdot\frac{k_4}{k_5-k_4} & 1 \end{bmatrix}. \tag{32}$$

3. Applications

The purpose of this section is to demonstrate the decomposition method using text-book parameters rather than to model a specific reactive transport system. The first-order decay rates and half lives of selected species are selected and assumed as listed in Table 1 (Peterson et al., 2007).

Table 1. Half Lives and Decay Rates

Species Number	Figure	Half-life	Decay Rate (yr^{-1})
1	6	900 y	7.702×10^{-4}
4	8	13 y	5.332×10^{-2}
1	8	6900 y	1.005×10^{-4}
2	8	3.2 h	1.899×10^{3}
4	6	1400 y	4.951×10^{-4}
2	6	16 My	4.332×10^{-8}
5	8	39 m	9.348×10^{3}
6	8	4700 y	1.475×10^{-4}
3	8	11 d	2.302×10^{1}
7	6	29 y	2.390×10^{-2}
3	6	5 h	1.215×10^{3}
5	6	7400 y	9.367×10^{-5}
1	3	150 y	4.621×10^{-3}
3	3	160 d	1.582
7	8	380000 y	1.824×10^{-6}
6	6	2.4 d	1.055×10^{2}
8	6	24000 y	2.888×10^{-5}
2	3	2.1 d	1.206×10^{2}
4	3	88 y	7.877×10^{-3}
8	8	4.46 By	1.55414×10^{-10}
9	6	710 My	9.76264×10^{-10}
5	3	246000 y	2.81767×10^{-05}

$k = \ln(2)/t_{1/2}$, where $t_{1/2}$ is the half-life time.
The time units are defined as: y: years; My: million years; By: billion years; m: minuets; h: hours; d: days.

3.1. Radioactive Decay Networks in Batch Reactors

In this subsection, we consider radioactive decay networks in the spatial-independent systems, such as a rock sample or a batch reactor. As shown in Figure 3, the yield (branching) factor from species 1 to species 2 is 0.5%. The matrices $\mathbf{S}^-$ and $\mathbf{S}$, Eqs. (13) and (14), of the converging decay network (3), are modified accordingly to Eqs. (15) and (16). Then, the solution of the decay network, $\mathbf{c} = \mathbf{S}\ \exp(\mathbf{\Lambda} t)\ [\mathbf{S}^- \mathbf{c}^o]$, can be explicitly expressed as

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{\alpha k_1}{k_2-k_1} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{\alpha k_1}{k_4-k_1}\cdot\frac{k_2}{k_2-k_1} & \frac{k_2}{k_4-k_2} & \frac{k_3}{k_4-k_3} & 1 & 0 \\ \frac{\alpha k_1}{k_5-k_1}\cdot\frac{k_2}{k_2-k_1}\cdot\frac{k_4}{k_4-k_1} & \frac{k_2}{k_5-k_2}\cdot\frac{k_4}{k_4-k_2} & \frac{k_3}{k_5-k_3}\cdot\frac{k_4}{k_4-k_3} & \frac{k_4}{k_5-k_4} & 1 \end{bmatrix}$$

$$\times \begin{bmatrix} e^{-k_1 t} & 0 & 0 & 0 & 0 \\ 0 & e^{-k_2 t} & 0 & 0 & 0 \\ 0 & 0 & e^{-k_3 t} & 0 & 0 \\ 0 & 0 & 0 & e^{-k_4 t} & 0 \\ 0 & 0 & 0 & 0 & e^{-k_5 t} \end{bmatrix}$$

$$\times \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{\alpha k_1}{k_1-k_2} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \frac{\alpha k_1}{k_1-k_4}\cdot\frac{k_2}{k_2-k_4} & \frac{k_2}{k_2-k_4} & \frac{k_3}{k_3-k_4} & 1 & 0 \\ \frac{\alpha k_1}{k_1-k_5}\cdot\frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_2}{k_2-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_3}{k_3-k_5}\cdot\frac{k_4}{k_4-k_5} & \frac{k_4}{k_4-k_5} & 1 \end{bmatrix} \begin{bmatrix} c_1^o \\ c_2^o \\ c_3^o \\ c_4^o \\ c_5^o \end{bmatrix}. \quad (33)$$

If the initial concentrations of species 1 and 3 are assumed to be 1, the relative concentration profiles are calculated using the analytical solution (33), ode45 (the nonstiff ODE solver, Mathworks, 2000), and ode23s (the stiff ODE solver, Mathworks, 2000) with default values of relative and absolute error tolerances (1×10^{-3} and 1×10^{-6}). Because of the contrast decay rates between species 4 and 5, the ode45 fails to produce converged results. The concentrations calculated using the analytical solution and ode23s are compared as shown in Figure 5. Although the numerical solution is seen to be essentially identical to the analytical one, it requires 47 times more CPU time.

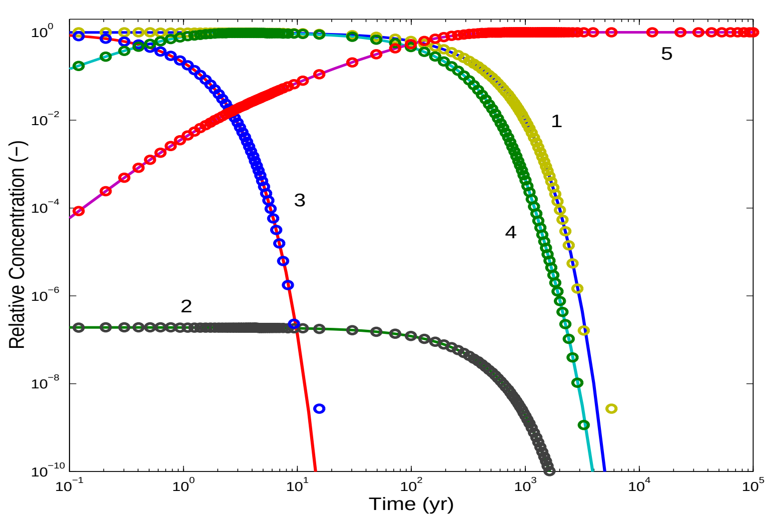

Figure 5. Relative concentrations of species in the converging decay network of Figure 3 as functions of time. Circles and solid lines, respectively, represent numerical (using matlab ode23s) and the analytical solution (Eq. 33).

In addition to the demonstration of the single-converging (Figure 3) decay network, we further apply the matrix decomposition to a double-converging network. As shown in Figure 6, species 3 and 4 decay to produce a single daughter product, species 5, and species 6 and 7 decay to produce species 8. The corresponding transformation matrices are derived using Eqs. (6) and (7) as shown in Appendix A.

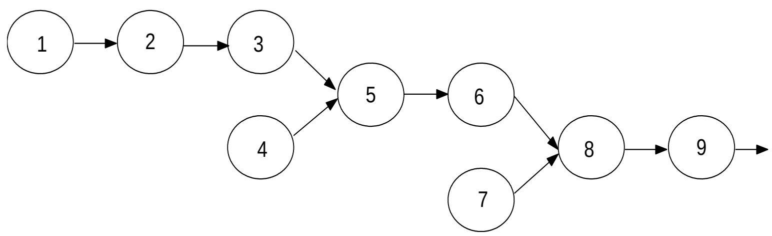

Figure 6. A double converging decay network (Peterson et al., 2007).

When the initial concentrations of three original species (1, 4, and 7) are assumed to be one, the relative concentrations of all species are calculated as shown in Figure 7.

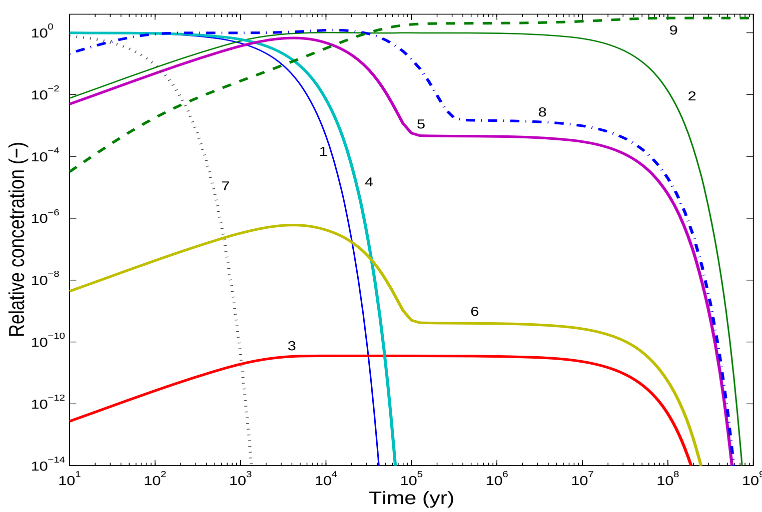

Figure 7. Species concentrations in the double converging decay network of Figure 6.

Figure 8 is a typical example with sequential, multi-parent converging, and multi-daughter branching structure. In the decay network, a large contrast in the half lives between species 5 (39 minutes) and species 7 (380,000 yrs) cause the ODE system to be stiff.

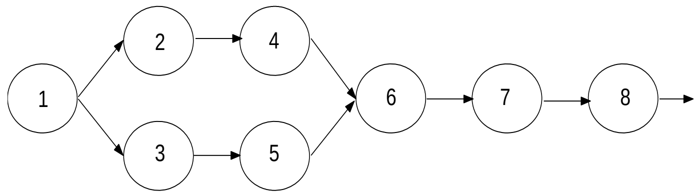

Figure 8. A sequential, branching, and converging decay network.

Using Eqs. (15) and (16), the transformation matrices $\mathbf{S}^{-}$ and $\mathbf{S}$ are derived as shown in Appendix B. The concentration profiles, relative to the first species concentration, are calculated in Figure 9.

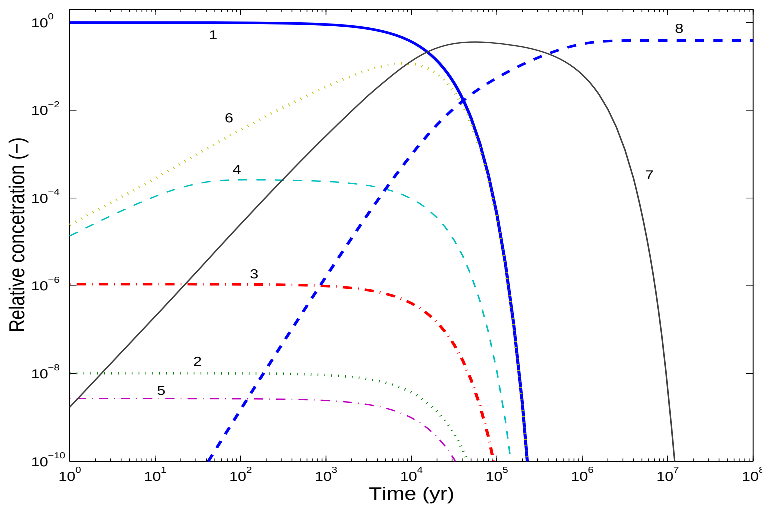

Figure 9. Species concentrations in the sequential, branching, and converging decay network of Figure 8.

3.2. Transport Coupled With Decay Networks

The decomposition concept and methodology are applicable to reactive transport systems. If the analytical solution of a single-species transport with first-order decay is available, the solution can be expanded to the transport of coupled reaction networks. For example, the standard analytical solution of Bear (1979, p.~268) for transport in a semi-infinite column can be applied to each independent subsystem in the transformed domain as

$$a_i = a_i^o f_i, \quad \forall i = 1, 2, \cdots, M \tag{34}$$

where a_i^o is the boundary concentration in the transformed domain ($\mathbf{a}^o = \mathbf{S}^{-}\mathbf{c}^o$), $\mathbf{c}^o$ is the vector of the boundary concentrations,

$$f_i = \frac{1}{2}\exp\left(\frac{vx}{2D}\right)\left[\exp(-\beta_i x)\mathrm{erfc}\gamma_i^{-} + \exp(\beta_i x)\mathrm{erfc}\gamma_i^{+}\right], \tag{35}$$

$$\beta_i = \left(\frac{v^2}{4D^2} + \frac{k_i}{D}\right)^{1/2}, \quad \mathrm{erfc}(\eta) = 1 - \mathrm{erf}(\eta) = \frac{2}{\sqrt{\pi}}\int_{\eta}^{\infty}\exp(-\tau^2)d\tau,$$

$$\gamma_i^- = \frac{x - (v + 4k_i D)^{1/2} t}{2(Dt)^{1/2}}, \quad \gamma_i^+ = \frac{x + (v + 4k_i D)^{1/2} t}{2(Dt)^{1/2}}, \quad \forall i = 1, 2, \cdots, M.$$

In Eq. (35), x [L] is the distance, v [LT^{-1}] and D [$\mathrm{L}^2\mathrm{T}^{-1}$] are flow velocity and dispersion coefficient. Using $\mathbf{c} = \mathbf{S}\ \mathbf{a}$, the solution of the reactive transport system in the "c" domain is expressed analytically. The concentrations of the converging network (Figure 3) are calculated, as functions of distance at 50 and 100 years, as shown in Figure 10.

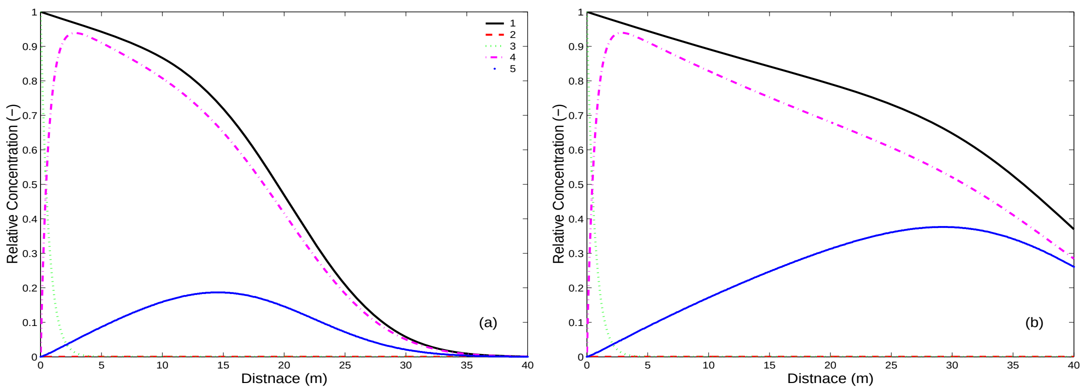

Figure 10. Spatial concentration distribution in the converging decay network of Figure 3 as functions of distance at (a) 50 and (b) 100 years. $v = 0.4$ m/yr and $D = 0.4$ m^2/yr. Note that low values of velocity and dispersion coefficient are used to demonstrate the decay reactions and to exaggerate daughter species concentrations.

4. Discussion and Conclusions

A generalized decomposition method has been developed and mathematically formulated for a wide range of first-order decay networks. The method can be used for systematically deriving closed-form solutions of first-order reactions. Then, the closed-form solutions can be coupled with transport in the operator-splitting scheme. Through benchmark problems, it is shown that the generalized decomposition method is computationally efficient, accurate, and robust.

The decomposition method has been demonstrated using sequential, converging, branching decay networks. For comparison purposes, the generalized decomposition process is developed for the single-parent and single-daughter decay chain (sequential) and the derived transformation matrices are identical to those derived using singular value decomposition (Sun et al., 1999). The transformation matrices of complex reaction networks are derived accordingly to the relative position in the decay network. Using the analogy of a generic family tree, the behavior of a daughter product comes from parent species and all ancestors. A component of transformation matrices represents the relationship between the daughter species and its ancestor. The relationship is quantified using the first-order decay rates and branching factors.

Although the exact solution of a decay network provides more accurate simulation results, the decay rates are uncertain in reality. The uncertainty of decay rates can be propagated and accumulated from parent to daughter species. The proposed solution scheme, which requires much less computational effort, is ideal for quantifying the uncertainties and evaluating uncertainty propagation.

Compromise is often made by modelers between transport and reactions. In order to facilitate the simulation of reaction networks, flow and transport are often simplified. Sometimes, when transport is focused, reaction networks have to be treated as unrelated species. Since the proposed method provides exact solutions for reactions with single-step calculations, for a given computational effort, transport can be modeled in greater detail.

Acknowledgements

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Appendix A: Transformation Matrices of Figure 6 Decay Network

Transformation matrices $\mathbf{S}^-$ and $\mathbf{S}$ of Figure 6 decay network are formulated as:

$$\mathbf{S}^- = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_1-k_2} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ S^-_{3,1} & \frac{k_2}{k_2-k_3} & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ S^-_{5,1} & S^-_{5,2} & \frac{k_3}{k_3-k_5} & \frac{k_4}{k_4-k_5} & 1 & 0 & 0 & 0 & 0 \\ S^-_{6,1} & S^-_{6,2} & S^-_{6,3} & S^-_{6,4} & \frac{k_5}{k_5-k_6} & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ S^-_{8,1} & S^-_{8,2} & S^-_{8,3} & S^-_{8,4} & S^-_{8,5} & \frac{k_6}{k_6-k_8} & \frac{k_7}{k_7-k_8} & 1 & 0 \\ S^-_{9,1} & S^-_{9,2} & S^-_{9,3} & S^-_{9,4} & S^-_{9,5} & S^-_{9,6} & S^-_{9,7} & \frac{k_8}{k_8-k_9} & 1 \end{bmatrix} \tag{36}$$

$$S^-_{3,1} = \frac{k_1}{k_1-k_3} \cdot \frac{k_2}{k_2-k_3}$$

$$S^-_{5,1} = \frac{k_1}{k_1-k_5} \cdot \frac{k_2}{k_2-k_5} \cdot \frac{k_3}{k_3-k_5}, \quad S^-_{5,2} = \frac{k_2}{k_2-k_5} \cdot \frac{k_3}{k_3-k_5}$$

$$S^-_{6,1} = \frac{k_1}{k_1-k_6} \cdot \frac{k_2}{k_2-k_6} \cdot \frac{k_3}{k_3-k_6} \cdot \frac{k_5}{k_5-k_6}, \quad S^-_{6,2} = \frac{k_2}{k_2-k_6} \cdot \frac{k_3}{k_3-k_6} \cdot \frac{k_5}{k_5-k_6}$$

$$S^-_{6,3} = \frac{k_3}{k_3-k_6} \cdot \frac{k_5}{k_5-k_6}, \quad S^-_{6,4} = \frac{k_4}{k_4-k_6} \cdot \frac{k_5}{k_5-k_6}$$

$$S^-_{8,1} = \frac{k_1}{k_1-k_8} \cdot \frac{k_2}{k_2-k_8} \cdot \frac{k_3}{k_3-k_8} \cdot \frac{k_5}{k_5-k_8} \cdot \frac{k_6}{k_6-k_8}$$

$$S^-_{8,2} = \frac{k_2}{k_2-k_8} \cdot \frac{k_3}{k_3-k_8} \cdot \frac{k_5}{k_5-k_8} \cdot \frac{k_6}{k_6-k_8}, \quad S^-_{8,3} = \frac{k_3}{k_3-k_8} \cdot \frac{k_5}{k_5-k_8} \cdot \frac{k_6}{k_6-k_8}$$

$$S^-_{8,4} = \frac{k_4}{k_4-k_8} \cdot \frac{k_5}{k_5-k_8} \cdot \frac{k_6}{k_6-k_8}, \quad S^-_{8,5} = \frac{k_5}{k_5-k_8} \cdot \frac{k_6}{k_6-k_8}$$

$$S^-_{9,1} = \frac{k_1}{k_1-k_9} \cdot \frac{k_2}{k_2-k_9} \cdot \frac{k_3}{k_3-k_9} \cdot \frac{k_5}{k_5-k_9} \cdot \frac{k_6}{k_6-k_9} \cdot \frac{k_8}{k_8-k_9}$$

$$S^-_{9,2} = \frac{k_2}{k_2-k_9} \cdot \frac{k_3}{k_3-k_9} \cdot \frac{k_5}{k_5-k_9} \cdot \frac{k_6}{k_6-k_9} \cdot \frac{k_8}{k_8-k_9}$$

$$S^{-}_{9,3} = \frac{k_3}{k_3 - k_9} \cdot \frac{k_5}{k_5 - k_9} \cdot \frac{k_6}{k_6 - k_9} \cdot \frac{k_8}{k_8 - k_9}, \quad S^{-}_{9,4} = \frac{k_4}{k_4 - k_9} \cdot \frac{k_5}{k_5 - k_9} \cdot \frac{k_6}{k_6 - k_9} \cdot \frac{k_8}{k_8 - k_9}$$

$$S^{-}_{9,5} = \frac{k_5}{k_5 - k_9} \cdot \frac{k_6}{k_6 - k_9} \cdot \frac{k_8}{k_8 - k_9}, \quad S^{-}_{9,6} = \frac{k_6}{k_6 - k_9} \cdot \frac{k_8}{k_8 - k_9}, \quad S^{-}_{9,7} = \frac{k_7}{k_7 - k_9} \cdot \frac{k_8}{k_8 - k_9}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ S_{3,1} & \frac{k_2}{k_3 - k_2} & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ S_{5,1} & S_{5,2} & \frac{k_3}{k_5 - k_3} & \frac{k_4}{k_5 - k_4} & 1 & 0 & 0 & 0 & 0 \\ S_{6,1} & S_{6,2} & S_{6,3} & S_{6,4} & \frac{k_5}{k_6 - k_5} & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ S_{8,1} & S_{8,2} & S_{8,3} & S_{8,4} & S_{8,5} & \frac{k_6}{k_8 - k_6} & \frac{k_7}{k_8 - k_7} & 1 & 0 \\ S_{9,1} & S_{9,2} & S_{9,3} & S_{9,4} & S_{9,5} & S_{9,6} & S_{9,7} & \frac{k_8}{k_9 - k_8} & 1 \end{bmatrix} \tag{37}$$

$$S_{3,1} = \frac{k_1}{k_3 - k_1} \cdot \frac{k_2}{k_2 - k_1}$$

$$S_{5,1} = \frac{k_1}{k_5 - k_1} \cdot \frac{k_2}{k_2 - k_1} \cdot \frac{k_3}{k_3 - k_1}, \quad S_{5,2} = \frac{k_2}{k_5 - k_2} \cdot \frac{k_3}{k_3 - k_2}$$

$$S_{6,1} = \frac{k_1}{k_6 - k_1} \cdot \frac{k_2}{k_2 - k_1} \cdot \frac{k_3}{k_3 - k_1} \cdot \frac{k_5}{k_5 - k_1}, \quad S_{6,2} = \frac{k_2}{k_6 - k_2} \cdot \frac{k_3}{k_3 - k_2} \cdot \frac{k_5}{k_5 - k_2}$$

$$S_{6,3} = \frac{k_3}{k_6 - k_3} \cdot \frac{k_5}{k_5 - k_3}, \quad S_{6,4} = \frac{k_4}{k_6 - k_4} \cdot \frac{k_5}{k_5 - k_4}$$

$$S_{8,1} = \frac{k_1}{k_8 - k_1} \cdot \frac{k_2}{k_2 - k_1} \cdot \frac{k_3}{k_3 - k_1} \cdot \frac{k_5}{k_5 - k_1} \cdot \frac{k_6}{k_6 - k_1}$$

$$S_{8,2} = \frac{k_2}{k_8 - k_2} \cdot \frac{k_3}{k_3 - k_2} \cdot \frac{k_5}{k_5 - k_2} \cdot \frac{k_6}{k_6 - k_2}, \quad S_{8,3} = \frac{k_3}{k_8 - k_3} \cdot \frac{k_5}{k_5 - k_3} \cdot \frac{k_6}{k_6 - k_3}$$

$$S_{8,4} = \frac{k_4}{k_8 - k_4} \cdot \frac{k_5}{k_5 - k_4} \cdot \frac{k_6}{k_6 - k_4}, \quad S_{8,5} = \frac{k_5}{k_8 - k_5} \cdot \frac{k_6}{k_6 - k_5}$$

$$S_{9,1} = \frac{k_1}{k_9 - k_1} \cdot \frac{k_2}{k_2 - k_1} \cdot \frac{k_3}{k_3 - k_1} \cdot \frac{k_5}{k_5 - k_1} \cdot \frac{k_6}{k_6 - k_1} \cdot \frac{k_8}{k_8 - k_1}$$

$$S_{9,2} = \frac{k_2}{k_9 - k_2} \cdot \frac{k_3}{k_3 - k_2} \cdot \frac{k_5}{k_5 - k_2} \cdot \frac{k_6}{k_6 - k_2} \cdot \frac{k_8}{k_8 - k_2}$$

$$S_{9,3} = \frac{k_3}{k_9 - k_3} \cdot \frac{k_5}{k_5 - k_3} \cdot \frac{k_6}{k_6 - k_3} \cdot \frac{k_8}{k_8 - k_3}, \quad S_{9,4} = \frac{k_4}{k_9 - k_4} \cdot \frac{k_5}{k_5 - k_4} \cdot \frac{k_6}{k_6 - k_4} \cdot \frac{k_8}{k_8 - k_4}$$

$$S_{9,5} = \frac{k_5}{k_9 - k_5} \cdot \frac{k_6}{k_6 - k_5} \cdot \frac{k_8}{k_8 - k_5}, \quad S_{9,6} = \frac{k_6}{k_9 - k_6} \cdot \frac{k_8}{k_8 - k_6}, \quad S_{9,7} = \frac{k_7}{k_9 - k_7} \cdot \frac{k_8}{k_8 - k_7}.$$

Appendix B: Transformation Matrices of Figure 8 Decay Network

Transformation matrices $\mathbf{S}^-$ and $\mathbf{S}$ of Figure 8 decay network are formulated as:

$$\mathbf{S}^- = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\alpha_1 k_1}{k_1-k_2} & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\alpha_2 k_1}{k_1-k_3} & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ S^-_{4,1} & S^-_{4,2} & 0 & 1 & 0 & 0 & 0 & 0 \\ S^-_{5,1} & 0 & \frac{k_3}{k_3-k_5} & 0 & 1 & 0 & 0 & 0 \\ S^-_{6,1} & S^-_{6,2} & S^-_{6,3} & \frac{k_4}{k_4-k_6} & \frac{k_5}{k_5-k_6} & 1 & 0 & 0 \\ S^-_{7,1} & S^-_{7,2} & S^-_{7,3} & S^-_{7,4} & S^-_{7,5} & \frac{k_6}{k_6-k_7} & 1 & 0 \\ S^-_{8,1} & S^-_{8,2} & S^-_{8,3} & S^-_{8,4} & S^-_{8,5} & S^-_{8,6} & \frac{k_7}{k_7-k_8} & 1 \end{bmatrix} \tag{38}$$

$$S^-_{4,1} = \frac{\alpha_1 k_1}{k_1-k_4}\cdot\frac{k_2}{k_2-k_4}, \quad S^-_{5,1} = \frac{\alpha_2 k_1}{k_1-k_5}\cdot\frac{k_3}{k_3-k_5}$$

$$S^-_{6,1} = \frac{k_1}{k_1-k_6}\left[\frac{\alpha_1 k_2}{k_2-k_6}\cdot\frac{k_4}{k_4-k_6} + \frac{\alpha_2 k_3}{k_3-k_6}\cdot\frac{k_5}{k_5-k_6}\right]$$

$$S^-_{6,2} = \frac{k_2}{k_2-k_6}\cdot\frac{k_4}{k_4-k_6}, \quad S^-_{6,3} = \frac{k_3}{k_3-k_6}\cdot\frac{k_5}{k_5-k_6}$$

$$S^-_{7,1} = \frac{k_1}{k_1-k_7}\cdot\left[\frac{\alpha_1 k_2}{k_2-k_7}\cdot\frac{k_4}{k_4-k_7} + \frac{\alpha_2 k_3}{k_3-k_7}\cdot\frac{k_5}{k_5-k_7}\right]\frac{k_6}{k_6-k_7}$$

$$S^-_{7,2} = \frac{k_2}{k_2-k_7}\cdot\frac{k_4}{k_4-k_7}\cdot\frac{k_6}{k_6-k_7}, \quad S^-_{7,3} = \frac{k_3}{k_3-k_7}\cdot\frac{k_5}{k_5-k_7}\cdot\frac{k_6}{k_6-k_7}$$

$$S^-_{7,4} = \frac{k_4}{k_4-k_7}\cdot\frac{k_6}{k_6-k_7}, \quad S^-_{7,5} = \frac{k_5}{k_5-k_7}\cdot\frac{k_6}{k_6-k_7}$$

$$S^-_{8,1} = \frac{k_1}{k_1-k_8}\left[\frac{\alpha_1 k_2}{k_2-k_8}\cdot\frac{k_4}{k_4-k_8} + \frac{\alpha_2 k_3}{k_3-k_8}\cdot\frac{k_5}{k_5-k_8}\right]\frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}$$

$$S^-_{8,2} = \frac{k_2}{k_2-k_8}\cdot\frac{k_4}{k_4-k_8}\cdot\frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}, \quad S^-_{8,3} = \frac{k_3}{k_3-k_8}\cdot\frac{k_5}{k_5-k_8}\cdot\frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}$$

$$S^-_{8,4} = \frac{k_4}{k_4-k_8}\cdot\frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}, \quad S^-_{8,5} = \frac{k_5}{k_5-k_8}\cdot\frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}, \quad S^-_{8,6} = \frac{k_6}{k_6-k_8}\cdot\frac{k_7}{k_7-k_8}$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\alpha_1 k_1}{k_2-k_1} & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\alpha_2 k_1}{k_3-k_1} & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ S_{4,1} & S_{4,2} & 0 & 1 & 0 & 0 & 0 & 0 \\ S_{5,1} & 0 & \frac{k_3}{k_5-k_3} & 0 & 1 & 0 & 0 & 0 \\ S_{6,1} & S_{6,2} & S_{6,3} & \frac{k_4}{k_6-k_4} & \frac{k_5}{k_6-k_5} & 1 & 0 & 0 \\ S_{7,1} & S_{7,2} & S_{7,3} & S_{7,4} & S_{7,5} & \frac{k_6}{k_7-k_6} & 1 & 0 \\ S_{8,1} & S_{8,2} & S_{8,3} & S_{8,4} & S_{8,5} & S_{8,6} & \frac{k_7}{k_8-k_7} & 1 \end{bmatrix} \tag{39}$$

$$S_{4,1} = \frac{k_1}{k_4-k_1}\cdot\frac{\alpha_1 k_2}{k_2-k_1}, \quad S_{5,1} = \frac{k_1}{k_5-k_1}\cdot\frac{\alpha_2 k_3}{k_3-k_1}$$

$$S_{6,1} = \frac{k_1}{k_6 - k_1}\left[\frac{\alpha_1 k_2}{k_2 - k_1}\cdot\frac{k_4}{k_4 - k_1} + \frac{\alpha_2 k_3}{k_3 - k_1}\cdot\frac{k_5}{k_5 - k_1}\right]$$

$$S_{6,2} = \frac{k_2}{k_6 - k_2}\cdot\frac{k_4}{k_4 - k_2}, \quad S_{6,3} = \frac{k_3}{k_6 - k_3}\cdot\frac{k_5}{k_5 - k_3}$$

$$S_{7,1} = \frac{k_1}{k_7 - k_1}\left[\frac{\alpha_1 k_2}{k_2 - k_1}\cdot\frac{k_4}{k_4 - k_1} + \frac{\alpha_2 k_3}{k_3 - k_1}\cdot\frac{k_5}{k_5 - k_1}\right]\frac{k_6}{k_6 - k_1}$$

$$S_{7,2} = \frac{k_2}{k_7 - k_2}\cdot\frac{k_4}{k_4 - k_2}\cdot\frac{k_6}{k_6 - k_2}, \quad S_{7,3} = \frac{k_3}{k_7 - k_3}\cdot\frac{k_5}{k_5 - k_3}\cdot\frac{k_6}{k_6 - k_3}$$

$$S_{7,4} = \frac{k_4}{k_7 - k_4}\cdot\frac{k_6}{k_6 - k_4}, \quad S_{7,5} = \frac{k_5}{k_7 - k_5}\cdot\frac{k_6}{k_6 - k_5}$$

$$S_{8,1} = \frac{k_1}{k_8 - k_1}\left[\frac{\alpha_1 k_2}{k_2 - k_1}\cdot\frac{k_4}{k_4 - k_1} + \frac{\alpha_2 k_3}{k_3 - k_1}\cdot\frac{k_5}{k_5 - k_1}\right]\frac{k_6}{k_6 - k_1}\cdot\frac{k_7}{k_7 - k_1}$$

$$S_{8,2} = \frac{k_2}{k_8 - k_2}\cdot\frac{k_4}{k_4 - k_2}\cdot\frac{k_6}{k_6 - k_2}\cdot\frac{k_7}{k_7 - k_2}, \quad S_{8,3} = \frac{k_3}{k_8 - k_3}\cdot\frac{k_5}{k_5 - k_3}\cdot\frac{k_6}{k_6 - k_3}\cdot\frac{k_7}{k_7 - k_3}$$

$$S_{8,4} = \frac{k_4}{k_8 - k_4}\cdot\frac{k_6}{k_6 - k_4}\cdot\frac{k_7}{k_7 - k_4}, \quad S_{8,5} = \frac{k_5}{k_8 - k_5}\cdot\frac{k_6}{k_6 - k_5}\cdot\frac{k_7}{k_7 - k_5}, \quad S_{8,6} = \frac{k_6}{k_8 - k_6}\cdot\frac{k_7}{k_7 - k_6}.$$

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