Examining the Accuracy of Methods for Obtaining Pressure Dependent Rate Coefficients

Supplementary Information

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1 CSE Derivations

$$\frac{d\mathbf{p}}{dt} = \mathbf{G}\mathbf{p} + \sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) \mathbf{f}_{\nu} \tag{1}$$

where

$$\mathbf{f}_{\nu} = \mathbf{k}_{\nu\rightarrow}\mathbf{b}_{\nu} \tag{2}$$

where $\mathbf{k}_{\nu\rightarrow}$ is the vector of loss coefficients from ν to every other element of $\mathbf{p}$ and $\mathbf{b}_{\nu}$ is defined by

$$\mathbf{b}_{\nu_i} = \frac{\rho_{\nu}(E(i)) e^{\frac{-E(i)}{RT}}}{\sum_{j}^{N_{grains}} \rho_{\nu}(E_j) e^{\frac{-E_j}{RT}}} \tag{3}$$

where ρ_v is the density of states, $E(i)$ is the energy of the corresponding element of $\mathbf{p}$, E_j is the jth energy level, R is the gas constant and T is the temperature. Eigendecomposing $\mathbf{G}$ gives us eigenmatrix $\mathbf{Q}$ such that

$$\mathbf{\Lambda} = \mathbf{Q}^{-1}\mathbf{G}\mathbf{Q} \tag{4}$$

where $\mathbf{\Lambda}$ is diagonal with the eigenvalues of each eigenvector on the diagonal. if we define

$$\mathbf{v} = \mathbf{Q}^{-1}\mathbf{p} \tag{5}$$

we can transform Equation 1 into

$$\frac{d\mathbf{v}}{dt} = \mathbf{\Lambda}\mathbf{v} + \sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) \mathbf{Q}^{-1}\mathbf{f}_{\nu} \tag{6}$$

At steady state each element of Equation 6 can be written as

$$\mathbf{v}_i = -\frac{1}{\mathbf{\Lambda}_{ii}} \sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) [\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_i \tag{7}$$

while this isn't a good approximation for the values of the chemically significant eigenstates, it is a good approximation for the energy transfer associated eigenstates. We can write the flux to a particular bimolecular channel ν as the sum of each element of $\mathbf{p}$ times the rate coefficient from that element to ν utilizing coordinate invariance we have

$$r_{\to\mu} =< \mathbf{p}, \mathbf{k}_{\to\mu} >=< \mathbf{v}, \mathbf{Q}^{-1}\mathbf{k}_{\to\mu} > \tag{8}$$

where $\mathbf{k}_{\to\mu}$ is the vector of rate coefficients from each element of $\mathbf{p}$ to channel μ. As discussed in Georgievskii et al. 2013 the energy transfer associated components to Equation 8 are associated with bimolecular-bimolecular reactions while the chemically-significant eigenvalue components are associated with isomer-bimolecular reactions. Therefore, we can look specifically at the energy transfer associated components of Equation 8 and plug in Equation 7 to give

$$r_{\to\mu} = -\sum_{i}\sum_{\nu} \frac{1}{\mathbf{\Lambda}_{ii}} y_{A\nu}(t) y_{B\nu}(t) [\mathbf{Q}^{-1}\mathbf{k}_{\to\mu}]_i [\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_i \tag{9}$$

separating the component coming from each bimolecular input channel we get

$$k_{\nu\to\mu} y_{A\nu}(t) y_{B\nu}(t) = r_{\nu\to\mu} = -\sum_i \frac{1}{\mathbf{\Lambda}_{ii}} y_{A\nu}(t) y_{B\nu}(t) [\mathbf{Q}^{-1}\mathbf{k}_{\to\mu}]_i [\mathbf{Q}^{-1}\mathbf{f}_\nu]_i \tag{10}$$

giving us

$$k_{\nu\to\mu} = -\sum_i \frac{1}{\mathbf{\Lambda}_{ii}} [\mathbf{Q}^{-1}\mathbf{k}_{\to\mu}]_i [\mathbf{Q}^{-1}\mathbf{f}_\nu]_i \tag{11}$$

a formula for the bimolecular-bimolecular rate coefficients.

The remaining rate coefficients are derived from the chemically significant eigencomponents. We need rate coefficients of the form

$$\frac{d\mathbf{y}_i}{dt} = -\mathbf{y}_i \sum_j k_{i\to j} + \sum_{j\neq i} k_{j\to i}\mathbf{y}_j + \sum_\nu k_{\nu\to i} y_{A\nu} y_{B\nu} \tag{12}$$

where y_i is the total concentration of the ith isomer. In order to obtain $\mathbf{y}$ we need to translate the chemically significant eigenstates into total concentrations. We do this by energy summing the chemically significant eigenvectors

$$\mathbf{W}_{ij} = \sum_{k\in isomer\ i} \mathbf{Q}_{kj}\ j \in N_{cse} \tag{13}$$

generating a pseudo-eigenbasis for the chemical subspace. We can then define $\mathbf{v}_{cse}$ as the vector of chemically signficant eigenstates and write

$$\mathbf{y} \approx \mathbf{W}\mathbf{v}_{cse} \tag{14}$$

providing us a way to convert between total concentrations and the eigenstates. We can also rewrite Equation 6 as

$$\frac{d\mathbf{v}_{cse}}{dt} = \mathbf{\Lambda}_{cse}\mathbf{v}_{cse} + \sum_\nu y_{A\nu}(t) y_{B\nu}(t) [\mathbf{Q}^{-1}\mathbf{f}_\nu]_{cse} \tag{15}$$

Let us consider the flux between two isomers

$$r_{isomers \to j} = \sum_{j \neq i} k_{i \to j} \mathbf{y}_i = [\mathbf{W}\mathbf{\Lambda}\mathbf{v}_{cse}]_j \tag{16}$$

breaking this into components and expanding this into a matrix gives us

$$\mathbf{K}\mathbf{y} = \mathbf{W}\mathbf{\Lambda}\mathbf{v}_{cse} = \mathbf{W}\mathbf{\Lambda}\mathbf{W}^{-1}\mathbf{y} \tag{17}$$

where $\mathbf{K}$ is the matrix of isomerization rate coefficients giving us

$$k_{i \to j} = [\mathbf{W}\mathbf{\Lambda}\mathbf{W}^{-1}]_{ij} \tag{18}$$

a formula for the isomerization rate coefficients.

Comparing the bimolecular components of equations 12 and 15 we have

$$\sum_{\nu} k_{\nu \to i} y_{A\nu}(t) y_{B\nu}(t) = \big[\mathbf{W} \sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) \big[\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_{cse}\big]_i \tag{19}$$

expanding into a vector we get

$$\sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) \mathbf{k}_{\nu \to} = \sum_{\nu} y_{A\nu}(t) y_{B\nu}(t) \mathbf{W} \big[\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_{cse} \tag{20}$$

where $\mathbf{k}_{\nu \to}$ is the vector of rate constants from ν to every isomer and breaking into components gives us

$$\mathbf{k}_{\nu \to} = \mathbf{W} \big[\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_{cse} \tag{21}$$

or

$$k_{\nu \to i} = [\mathbf{W} \big[\mathbf{Q}^{-1}\mathbf{f}_{\nu}]_{cse}]_i \tag{22}$$

formulas for the bimolecular to isomer rate coefficients.

For the bimolecular to isomer rate coefficients we revisit Equation 8 and consider the sum component associated with the chemically significant eigenvectors

$$r_{\rightarrow\mu} = \sum_{i}^{N_{cse}} v_{cse_i} [\mathbf{Q}^{-1}\mathbf{k}_{\rightarrow\mu}]_i = \sum_{i}^{N_{cse}} [\mathbf{W}^{-1}\mathbf{y}]_i [\mathbf{Q}^{-1}\mathbf{k}_{\rightarrow\mu}]_i = \sum_{i}^{N_{cse}} [\mathbf{Q}^{-1}\mathbf{k}_{\rightarrow\mu}]_i \sum_{j} \mathbf{W}_{ij}^{-1}\mathbf{y}_j \tag{23}$$

breaking up into components we have

$$r_{j\rightarrow\mu} = \sum_{i}^{N_{cse}} [\mathbf{Q}^{-1}\mathbf{k}_{\rightarrow\mu}]_i \mathbf{W}_{ij}^{-1} y_j = k_{j\rightarrow\mu}\mathbf{y}_j \tag{24}$$

therefore we have

$$k_{j\rightarrow\mu} = \sum_{i}^{N_{cse}} [\mathbf{Q}^{-1}\mathbf{k}_{\rightarrow\mu}]_i \mathbf{W}_{ij}^{-1} \tag{25}$$

a formula for the isomer to bimolecular rate coefficients.