Modeling of geochemical processes

Non-homogenous systems

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Dynamic models

Non-homogenous system of differential equations

$$\frac{d\mathbf{x}}{dt} = \mathbf{A}\mathbf{x} + \mathbf{b}$$

Transformation to homogenous system by substitution!

$$\mathbf{A}^{-1}\frac{d\mathbf{x}}{dt} = \mathbf{x} + \mathbf{A}^{-1}\,\mathbf{b}$$

$$\mathbf{z} = \mathbf{x} + \mathbf{A}^{-1}\,\mathbf{b}$$

$$\mathbf{x} = \mathbf{z} - \mathbf{A}^{-1}\,\mathbf{b}$$

$$\frac{d\mathbf{z}}{dt} = \frac{d\mathbf{x}}{dt}$$

$$\frac{d\mathbf{z}}{dt} = \mathbf{A}\,(\mathbf{z} - \mathbf{A}^{-1}\,\mathbf{b}) + \mathbf{b}$$

$$\frac{d\mathbf{z}}{dt} = \mathbf{A}\,\mathbf{z}$$

$\mathbf{z} = e^{\mathbf{A}\,t}\,\mathbf{z}_0$ where $\mathbf{z}_0 = \mathbf{x}_0 + \mathbf{A}^{-1}\mathbf{b}$

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Re-substitution gives

$$\mathbf{x} + \mathbf{A}^{-1}\mathbf{b} = e^{\mathbf{A}\,t}\,(\mathbf{x}_0 + \mathbf{A}^{-1}\,\mathbf{b})$$

re-organization leads to

$$\mathbf{x} = e^{\mathbf{A}\,t}\,(\mathbf{x}_0 + \mathbf{A}^{-1}\,\mathbf{b}) - \mathbf{A}^{-1}\,\mathbf{b}$$

$$\mathbf{x} = e^{\mathbf{A}\,t}\,\mathbf{x}_0 + e^{\mathbf{A}\,t}\mathbf{A}^{-1}\,\mathbf{b} - \mathbf{A}^{-1}\,\mathbf{b}$$

Substituting for $e^{\mathbf{A}t}$ yields:

$$\mathbf{x} = \sum_i e^{\lambda_i\,t}\,\mathbf{U}_i\,\mathbf{x}_0 + \sum_i e^{\lambda_i\,t}\,\mathbf{U}_i\,\mathbf{A}^{-1}\,\mathbf{b} - \mathbf{A}^{-1}\,\mathbf{b}$$

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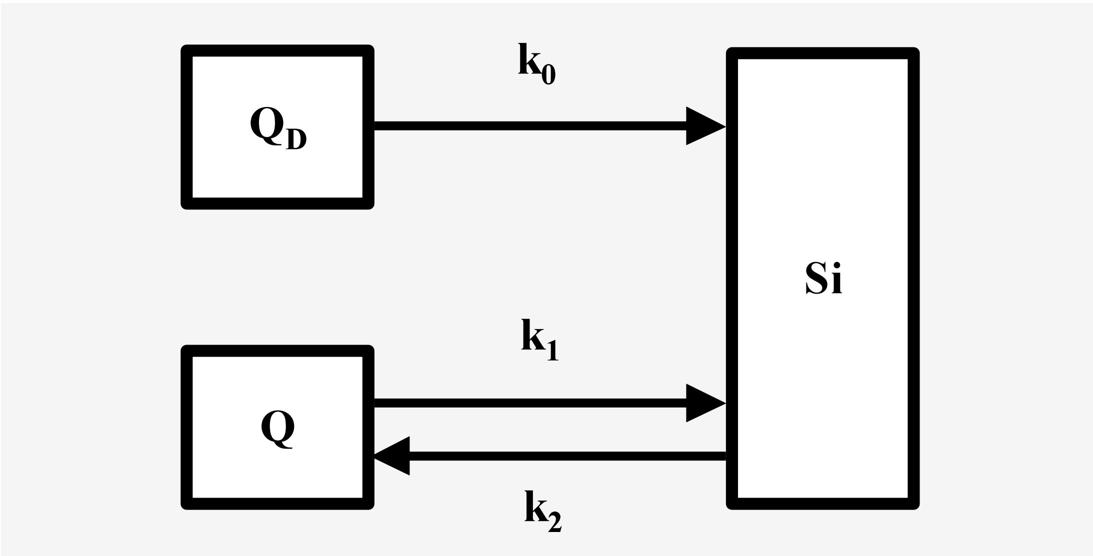
Example: Interaction quartz – water



Initial conditions:

$t = 0$

$[Si] = [Si]^0$

$Q_D = Q_D{}^0$

$Q = \text{const.}$

$$+\frac{dQ_D}{dt} = -k_0\,Q_D$$

$$+\frac{dn_{Si}}{dt} = k_0\,Q_D + k_1 Q - k_2\,\frac{n_{Si}}{V}$$

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Variables: $Q_D = x_1, \quad n_{Si} = x_2$

$$\frac{d}{dt}\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} -k_0 & 0 \\ k_0 & -\frac{k_2}{V} \end{bmatrix}\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} + \begin{bmatrix} 0 \\ k_1 Q \end{bmatrix}$$

$$\mathbf{A} = \begin{bmatrix} -k_0 & 0 \\ k_0 & -\frac{k_2}{V} \end{bmatrix} \qquad \det \mathbf{A} = \frac{k_0 k_2}{V}$$

$$\mathbf{A}^{-1} = \frac{V}{k_0 k_2}\begin{bmatrix} (-1)^{1+1}(-\frac{k_2}{V}) & (-1)^{1+2} k_0 \\ (-1)^{2+1} 0 & (-1)^{2+2}(-k_0) \end{bmatrix} = \begin{bmatrix} -\frac{1}{k_0} & 0 \\ -\frac{V}{k_2} & -\frac{V}{k_2} \end{bmatrix}$$

$$\frac{d\mathbf{x}}{dt} = \mathbf{Ax} + \mathbf{b}$$

Decomposition of $\mathbf{A}$: $\quad \mathbf{A} = \mathbf{U\Lambda}U^{-1}$

$$\det\begin{bmatrix} -k_0 - \lambda & 0 \\ k_0 & -\frac{k_2}{V} - \lambda \end{bmatrix} = 0$$

$$\lambda_2 = -\frac{k_2}{V}$$

$$\lambda_1 = -k_0$$

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$$\mathbf{A}\,\mathbf{u}_1 = \lambda_1\,\mathbf{u}_1$$

$$\begin{bmatrix} -k_0 & 0 \\ k_0 & -\frac{k_2}{V} \end{bmatrix} \begin{bmatrix} u_{11} \\ u_{21} \end{bmatrix} = -k_0 \begin{bmatrix} u_{11} \\ u_{21} \end{bmatrix}$$

$$-k_0\,u_{11} = -k_0\,u_{11}$$

$$k_0\,u_{11} - \frac{k_2}{V} u_{21} = -k_0\,u_{21}$$

$$\mathbf{A}\,\mathbf{u}_2 = \lambda_2\,\mathbf{u}_2$$

$$\begin{bmatrix} -k_0 & 0 \\ k_0 & -\frac{k_2}{V} \end{bmatrix} \begin{bmatrix} u_{12} \\ u_{22} \end{bmatrix} = -\frac{k_2}{V} \begin{bmatrix} u_{12} \\ u_{22} \end{bmatrix}$$

$$-k_0\,u_{12} = -\frac{k_2}{V} u_{12}$$

$$k_0\,u_{12} - \frac{k_2}{V} u_{22} = -\frac{k_2}{V} u_{22}$$

$$k_0\,u_{11} = \left(\frac{k_2}{V} - k_0\right) u_{21}$$

let $u_{21} = 1$

then $u_{11} = \frac{k_2 - k_0 V}{k_0 V}$

$$u_{12} = 0$$

choosing unitary vector gives: $u_{12}^2 + u_{22}^2 = 1$

$$u_{22} = 1$$

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$$\mathbf{U} = \begin{bmatrix} \dfrac{k_2 - k_0 V}{k_0 V} & 0 \\ 1 & 1 \end{bmatrix}$$

$$\det \mathbf{U} = \frac{k_2 - k_0 V}{k_0 V}$$

$$\mathbf{U}^{-1} = \frac{k_0 V}{k_2 - k_0 V} \begin{bmatrix} (-1)^2 .1 & (-1)^3 .1 \\ (-1)^3 .0 & (-1)^4 \dfrac{k_2 - k_0 V}{k_0 V} \end{bmatrix}^T$$

$$\mathbf{U}^{-1} = \begin{bmatrix} \dfrac{k_0 V}{k_2 - k_0 V} & -\dfrac{k_0 V}{k_2 - k_0 V} \\ 0 & 1 \end{bmatrix}^T$$

$$\mathbf{U}^{-1} = \begin{bmatrix} \dfrac{k_0 V}{k_2 - k_0 V} & 0 \\ -\dfrac{k_0 V}{k_2 - k_0 V} & 1 \end{bmatrix}$$

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$$\mathbf{U}_1 = \begin{bmatrix} \frac{k_2 - k_0 V}{k_0 V} \\ 1 \end{bmatrix} \begin{bmatrix} \frac{k_0 V}{k_2 - k_0 V} & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ \frac{k_0 V}{k_2 - k_0 V} & 0 \end{bmatrix}$$

$$\mathbf{U}_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \begin{bmatrix} -\frac{k_0 V}{k_2 - k_0 V} & 1 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ -\frac{k_0 V}{k_2 - k_0 V} & 1 \end{bmatrix}$$

In general: $$\mathbf{x} = \sum_i e^{\lambda_i t} \mathbf{U}_i \mathbf{x}_0 + \sum_i e^{\lambda_i t} \mathbf{U}_i \mathbf{A}^{-1} \mathbf{b} - \mathbf{A}^{-1} \mathbf{b}$$

For two dimensional system:

$$\mathbf{x} = e^{\lambda_1 t} \mathbf{U}_1 \mathbf{x}_0 + e^{\lambda_2 t} \mathbf{U}_2 \mathbf{x}_0 + \\ + e^{\lambda_1 t} \mathbf{U}_1 \mathbf{A}^{-1} \mathbf{b} + e^{\lambda_2 t} \mathbf{U}_2 \mathbf{A}^{-1} \mathbf{b} - \mathbf{A}^{-1} \mathbf{b}$$

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$$
\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = e^{-k_0 t} \begin{bmatrix} 1 & 0 \\ \dfrac{k_0 V}{k_2 - k_0 V} & 0 \end{bmatrix} \begin{bmatrix} x_1^0 \\ x_2^0 \end{bmatrix} + e^{-\frac{k_2}{V} t} \begin{bmatrix} 0 & 0 \\ -\dfrac{k_0 V}{k_2 - k_0 V} & 1 \end{bmatrix} \begin{bmatrix} x_1^0 \\ x_2^0 \end{bmatrix} +
$$

$$
+ e^{-k_0 t} \begin{bmatrix} 1 & 0 \\ \dfrac{k_0 V}{k_2 - k_0 V} & 0 \end{bmatrix} \begin{bmatrix} -\dfrac{1}{k_0} & 0 \\ -\dfrac{V}{k_2} & -\dfrac{V}{k_2} \end{bmatrix} \begin{bmatrix} 0 \\ k_1 Q \end{bmatrix} +
$$

$$
+ e^{-\frac{k_2}{V} t} \begin{bmatrix} 0 & 0 \\ -\dfrac{k_0 V}{k_2 - k_0 V} & 1 \end{bmatrix} \begin{bmatrix} -\dfrac{1}{k_0} & 0 \\ -\dfrac{V}{k_2} & -\dfrac{V}{k_2} \end{bmatrix} \begin{bmatrix} 0 \\ k_1 Q \end{bmatrix} -
$$

$$
- \begin{bmatrix} -\dfrac{1}{k_0} & 0 \\ -\dfrac{V}{k_2} & -\dfrac{V}{k_2} \end{bmatrix} \begin{bmatrix} 0 \\ k_1 Q \end{bmatrix}
$$

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$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = e^{-k_0 t} \begin{bmatrix} x_1^0 \\ \dfrac{k_0 V x_1^0}{k_2 - k_0 V} \end{bmatrix} + e^{-\frac{k_2}{V} t} \begin{bmatrix} 0 \\ -\dfrac{k_0 V x_1^0}{k_2 - k_0 V} + x_2^0 \end{bmatrix} +$$

$$+ e^{-k_0 t} \begin{bmatrix} 0 \\ 0 \end{bmatrix} + e^{-\frac{k_2}{V} t} \begin{bmatrix} 0 \\ -\dfrac{k_1 V Q}{k_2} \end{bmatrix} - \begin{bmatrix} 0 \\ -\dfrac{k_1 Q V}{k_2} \end{bmatrix}$$

$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} x_1^0 e^{-k_0 t} \\ \dfrac{k_0 V x_1^0}{k_2 - k_0 V} e^{-k_0 t} \end{bmatrix} + \begin{bmatrix} 0 \\ -\dfrac{k_0 V x_1^0}{k_2 - k_0 V} e^{-\frac{k_2}{V} t} + x_2^0 e^{-\frac{k_2}{V} t} \end{bmatrix} +$$

$$+ \begin{bmatrix} 0 \\ -\dfrac{k_1 V Q}{k_2} e^{-\frac{k_2}{V} t} \end{bmatrix} - \begin{bmatrix} 0 \\ -\dfrac{k_1 Q V}{k_2} \end{bmatrix}$$

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$$x_1 = x_1^0\, e^{-k_0 t}$$

$$x_2 = \frac{k_0 V x_1^0}{k_2 - k_0 V} e^{-k_0 t} - \frac{k_0 V x_1^0}{k_2 - k_0 V} e^{-\frac{k_2}{V} t} + x_2^0\, e^{-\frac{k_2}{V} t} - \frac{k_1 V Q}{k_2} e^{-\frac{k_2}{V} t} + \frac{k_1 Q V}{k_2}$$

$$x_1 = x_1^0\, e^{-k_0 t}$$

$$x_2 = \frac{k_1 Q V}{k_2}\left(1 - e^{-\frac{k_2}{V} t}\right) + x_2^0\, e^{-\frac{k_2}{V} t} + \frac{k_0 V x_1^0}{k_2 - k_0 V}\left(e^{-k_0 t} - e^{-\frac{k_2}{V} t}\right)$$

$$Q_D = Q_D^0\, e^{-k_0 t}$$

$$n_{Si} = \frac{k_1 Q V}{k_2}\left(1 - e^{-\frac{k_2}{V} t}\right) + n_{Si}^0\, e^{-\frac{k_2}{V} t} + \frac{k_0 V Q_D^0}{k_2 - k_0 V}\left(e^{-k_0 t} - e^{-\frac{k_2}{V} t}\right)$$

$$[Si] = \frac{k_1 Q}{k_2}\left(1 - e^{-\frac{k_2}{V} t}\right) + [Si]^0\, e^{-\frac{k_2}{V} t} + \frac{k_0 Q_D^0}{k_2 - k_0 V}\left(e^{-k_0 t} - e^{-\frac{k_2}{V} t}\right)$$