

Day 3: Matrix notation for reactions and rate equations; Classical matrix methods for systems of 1st order reactions

Matrix notation and linearly independent reaction sets

As noted before, we may write a general set of reactions as

$$\sum_{j=1}^N \alpha_{ij} A_j = 0, i = 1, M \quad (\alpha_{ij} < 0 \text{ for reactants, } > 0 \text{ for products})$$

where N is the number of species, M is the number of reactions, and α_{ij} is the stoichiometric coefficient of species j in reaction i .

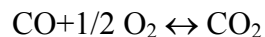
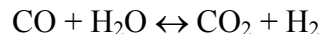
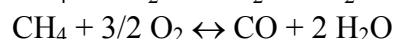
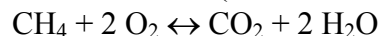
This may be written in matrix notation as

$$\underline{\underline{\alpha}} \underline{\underline{A}} = \underline{\underline{0}}$$

where $\underline{\underline{\alpha}}$ is the matrix of stoichiometric coefficients and $\underline{\underline{A}}$ is the vector of chemical species.

Example:

For the set of reactions (note that these are *not* elementary reactions)



we can define the vector of species as

$$\underline{\underline{A}} = \begin{bmatrix} \text{CH}_4 \\ \text{O}_2 \\ \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{CO} \\ \text{H}_2 \end{bmatrix}$$

then the matrix of stoichiometric coefficients is

$$\underline{\underline{\alpha}} = \begin{bmatrix} -1 & -2 & 1 & 2 & 0 & 0 \\ -1 & -3/2 & 0 & 2 & 1 & 0 \\ 0 & 0 & 1 & -1 & -1 & 1 \\ 0 & -1/2 & 1 & 0 & -1 & 0 \end{bmatrix}$$

In general, the reactions in a mechanism may not all be linearly independent. That is, some of the reactions may be linear combinations of others. The number of independent reactions is

equal to the *rank* of the matrix of stoichiometric coefficients. The rank may be found by performing elementary row operations – as you may have learned in a linear algebra class. For the example above, there are 3 independent reactions. Prove this to yourself. For a thermodynamic analysis (like determining the equilibrium composition) or for performing material balances it is almost always best to consider the minimal set of linearly independent reactions. For kinetic analysis and reactor simulation it is often better to include more than the linearly independent set. This is because we generally know the rate parameters for particular reactions. If we were to take linear combinations of these reactions, we would also have to take linear combinations of their rate expressions.

We may also define a vector of reaction rates \underline{r} and a vector of species concentrations \underline{C} so that the rate equations (as always during this first part of the course, for a well-mixed, constant volume system) are given by

$$\frac{d\underline{C}}{dt} = \underline{\alpha}^T \underline{r}$$

where $\underline{\alpha}^T$ is the transpose of the stoichiometric matrix.

For the example that we were just considering, this may be explicitly written as

$$\frac{d}{dt} \begin{bmatrix} C_{\text{CH}_4} \\ C_{\text{O}_2} \\ C_{\text{CO}_2} \\ C_{\text{H}_2\text{O}} \\ C_{\text{CO}} \\ C_{\text{H}_2} \end{bmatrix} = \begin{bmatrix} -1 & -1 & 0 & 0 \\ -2 & -\frac{3}{2} & 0 & -\frac{1}{2} \\ 1 & 0 & 1 & 1 \\ 2 & 2 & -1 & 0 \\ 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{bmatrix}$$

We could perform row operations on the transpose of the stoichiometric matrix to obtain the number of linearly independent reactions. That is also the number of linearly independent ordinary differential equations. If we used this minimal set of reactions, we would solve for linear combinations of species concentrations rather than for individual concentrations. For the example above, this could lead to the set of equations:

$$\frac{d}{dt} \begin{bmatrix} C_{\text{CH}_4} \\ C_{\text{CO}} \\ C_{\text{H}_2} \\ 2C_{\text{O}_2} + 2C_{\text{CO}_2} + C_{\text{CO}} + C_{\text{H}_2\text{O}} \\ C_{\text{CO}_2} + C_{\text{CH}_4} + C_{\text{CO}} \\ C_{\text{H}_2\text{O}} + 2C_{\text{CH}_4} + C_{\text{H}_2} \end{bmatrix} = \begin{bmatrix} -1 & -1 & 0 & 0 \\ 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{bmatrix}$$

After performing elementary row operations to eliminate everything below the diagonal of the transposed stoichiometric matrix, we are left with three ODE's for the CH_4 , CO , and H_2

concentrations. We have also discovered three *invariants* of the set of concentrations. These invariants are simply linear combinations of the concentrations that are independent of time. They are not unique – any linear combination of these invariants is also an invariant. They simply reflect the restrictions that the stoichiometry places on the concentration changes that can occur. For this example, the three invariants shown above physically correspond to conservation of O, C, and H atoms. For this example problem, we could now just integrate the three rate equations for CH₄, CO, and H₂, then solve for the other concentrations using the invariants.

Analytical solution for a network of 1st order reactions

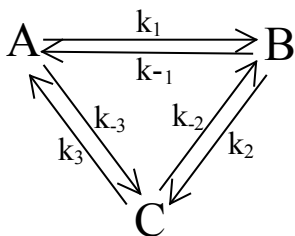
An arbitrary network of reactions that are all first order is something that we are rather *unlikely* to encounter in real life. However, we consider it in detail because (1) it is an elegant problem with an analytical solution, and more importantly (2) we may want to *linearize* the rate equations for reaction networks that include non-first-order reactions, in which case the linearized problem is identical to a network of first order reactions (it is a set of linear ordinary differential equations). This allows us to construct local solutions to nonlinear problems from analytical solutions to the linearized problem, and can provide insights into the local behavior of non-linear system of equations for which no analytical solution is possible.

For an arbitrary network of first-order reactions, the rate equations can be written:

$$\frac{d\underline{C}}{dt} = \underline{\underline{M}}\underline{C}$$

where \underline{C} is the vector of species concentrations and $\underline{\underline{M}}$ is a matrix of rate coefficients. The matrix $\underline{\underline{M}}$ a linear transformation of the stoichiometric matrix (i.e. one can construct a matrix $\underline{\underline{L}}$ such that $\underline{\underline{M}} = \underline{\underline{\alpha}}^T \underline{\underline{L}}$). However, it is generally more straightforward to construct $\underline{\underline{M}}$ directly. This is best illustrated by example.

Example: For the simple reaction network



The rate equations take the form

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 - k_{-3} & k_{-1} & k_3 \\ k_1 & -k_2 - k_{-1} & k_{-2} \\ k_{-3} & k_2 & -k_3 - k_{-2} \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

The general form of this for an arbitrary number of species is given in the textbook by Froment and Bischoff.

The general set of linear homogeneous ODE's with given initial conditions

$$\frac{d\underline{C}}{dt} = \underline{M}\underline{C}, \quad \underline{C}(t=0) = \underline{C}_o$$

has the same solution in matrix form as it has in scalar form. The solution is simply

$$\underline{C}(t) = \exp(\underline{M}t) \underline{C}_o$$

Of course, this requires that we know how to evaluate the exponential of a matrix. The exponential of a matrix is defined by its series expansion, just like the exponential of a scalar. That is

$$\exp(\underline{M}) = \underline{I} + \frac{1}{1!}\underline{M} + \frac{1}{2!}\underline{M}^2 + \frac{1}{3!}\underline{M}^3 + \frac{1}{4!}\underline{M}^4 + \frac{1}{5!}\underline{M}^5 + \dots$$

You can use this series expansion to demonstrate to yourself that the solution above satisfies the differential equation.

The exponential of a matrix can be written in terms of the eigenvectors and eigenvalues of the matrix. By definition, the eigenvalues and eigenvectors satisfy

$$\underline{M}\underline{x}_i = \lambda_i \underline{x}_i$$

where \underline{x}_i is the eigenvector corresponding to the i^{th} eigenvalue, λ_i .

Assembling the eigenvectors into a matrix gives

$$\underline{M}\underline{T} = \underline{\Lambda}\underline{T} \quad (= \underline{T}\underline{\Lambda})$$

where $\underline{\Lambda}$ is a diagonal matrix containing the eigenvalues of \underline{M} , and \underline{T} is the matrix whose columns are the corresponding eigenvectors of \underline{M} . Since $\underline{\Lambda}$ is diagonal, we can reverse the order of multiplication as shown above. Post-multiplying the above expression by \underline{T}^{-1} gives

$$\underline{M}\underline{T}\underline{T}^{-1} = \underline{M} = \underline{T}\underline{\Lambda}\underline{T}^{-1}$$

We can use this to show that \underline{M} raised to the n th power can be written as

$$\underline{M}^n = \underline{T}\underline{\Lambda}^n\underline{T}^{-1}$$

Substituting this result into the series expansion of the exponential function gives us

$$\begin{aligned} \exp(\underline{M}) &= \underline{I} + \frac{1}{1!}\underline{T}\underline{\Lambda}\underline{T}^{-1} + \frac{1}{2!}\underline{T}\underline{\Lambda}^2\underline{T}^{-1} + \frac{1}{3!}\underline{T}\underline{\Lambda}^3\underline{T}^{-1} + \frac{1}{4!}\underline{T}\underline{\Lambda}^4\underline{T}^{-1} + \frac{1}{5!}\underline{T}\underline{\Lambda}^5\underline{T}^{-1} + \dots \\ &= \underline{T}\left(\underline{I} + \frac{1}{1!}\underline{\Lambda} + \frac{1}{2!}\underline{\Lambda}^2 + \frac{1}{3!}\underline{\Lambda}^3 + \frac{1}{4!}\underline{\Lambda}^4 + \frac{1}{5!}\underline{\Lambda}^5 + \dots\right)\underline{T}^{-1} \\ &= \underline{T}\exp(\underline{\Lambda})\underline{T}^{-1} \end{aligned}$$

Substituting this result into our solution of the general set of linear homogeneous ODE's gives

$$\underline{C}(t) = (\underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1}) \underline{C}_o$$

Because $\underline{\Lambda}$ is diagonal, $\exp(\underline{\Lambda}t)$ is simply given by

$$\exp(\underline{\Lambda}t) = \begin{bmatrix} \exp(\lambda_1 t) & 0 & 0 & \dots \\ 0 & \exp(\lambda_2 t) & 0 & \dots \\ 0 & 0 & \exp(\lambda_3 t) & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix}$$

and we know how to evaluate that.

This eigenvector-eigenvalue analysis of a network of first order reactions is often called Wei-Prater analysis, after the originators of this treatment. It is discussed, from a slightly different point of view, beginning on p. 16 of Froment and Bischoff. The original paper is [Wei, J. and Prater, C.D., "The Structure and Analysis of Complex Reaction System.," in *Advances in Catalysis*, Vol. 13, Academic Press, New York (1962).]

An alternate (but equivalent) treatment of the network of 1st order reactions. This is more similar to what is in Froment and Bischoff, but using my notation (the same as that used above).

We have the set of equations

$$\frac{d\underline{C}}{dt} = \underline{M}\underline{C}, \quad \underline{C}(t=0) = \underline{C}_o$$

Again, the eigenvalues and eigenvectors of the matrix are defined such that

$$\underline{M}\underline{x}_i = \lambda_i \underline{x}_i$$

Assembling the eigenvectors into a matrix as above gives

$$\underline{M}\underline{T} = \underline{\Lambda}\underline{T}$$

Now, we use the eigenvectors to define a new vector that is made up of linear combinations of the concentrations

$$\underline{C} = \underline{T}\underline{y} \quad (\text{so } \underline{y} = \underline{T}^{-1}\underline{C})$$

Putting this in the equation gives

$$\frac{d\underline{T}\underline{y}}{dt} = \underline{M}\underline{T}\underline{y} = \underline{\Lambda}\underline{T}\underline{y} = \underline{T}\underline{\Lambda}\underline{y}, \quad \underline{y}(t=0) = \underline{y}_o \equiv \underline{T}^{-1}\underline{C}_o$$

Pre-multiplying both sides by \underline{T}^{-1} gives

$$\frac{d\underline{T}^{-1}\underline{T}\underline{y}}{dt} = \underline{T}^{-1}\underline{T}\underline{\Lambda}\underline{y}$$

or

$$\frac{d\underline{y}}{dt} = \underline{\Lambda}\underline{y}, \quad \underline{y}(t=0) = \underline{y}_o$$

which is the uncoupled set of scalar equations

$$\frac{dy_i}{dt} = \lambda_i y_i, \quad y_i(t=0) = y_{o,i}$$

Each scalar equation has the solution

$$y_i = \exp(\lambda_i t) y_{o,i}$$

Thus, in matrix form, the solution is

$$\underline{y} = \exp(\underline{\Lambda}t)\underline{y}_o$$

We can re-write this in terms of the actual concentrations as

$$\underline{\underline{T}}^{-1}\underline{\underline{C}} = \exp(\underline{\underline{\Lambda}}t)\underline{\underline{T}}^{-1}\underline{\underline{C}}_o$$

or, pre-multiplying by $\underline{\underline{T}}$

$$\underline{\underline{C}} = \underline{\underline{T}} \exp(\underline{\underline{\Lambda}}t)\underline{\underline{T}}^{-1}\underline{\underline{C}}_o$$

which is the same expression we obtained by the first method.

Returning to the example begun above for the three-component system, we can find the eigenvalues by solving

$$\det \begin{bmatrix} -k_1 - k_{-3} - \lambda & k_{-1} & k_3 \\ k_1 & -k_2 - k_{-1} - \lambda & k_{-2} \\ k_{-3} & k_2 & -k_3 - k_{-2} - \lambda \end{bmatrix} = 0$$

Multiplying out the determinant gives a cubic equation (the characteristic polynomial of the 3 by 3 matrix) that will have three roots (three solutions). These three roots are the three eigenvalues. Each of these eigenvalues can then be substituted into the equation that defines the eigenvalues and eigenvectors ($\underline{\underline{M}}\underline{\underline{x}}_i = \lambda_i \underline{\underline{x}}_i$), which can be solved to give the corresponding eigenvector. Note that the eigenvectors are only defined to within a multiplicative constant. That is, any multiple of an eigenvector is also an eigenvector. Omitting much algebra (that is conveniently performed by Maple or Mathematica) the eigenvalues are found to be (click [here](#) to download a Maple worksheet that does this)

$$\lambda_1 = 0$$

$$\lambda_2 = -\frac{1}{2}(k_1 + k_{-1} + k_2 + k_{-2} + k_3 + k_{-3} +$$

$$\frac{\sqrt{k_1^2 + k_{-1}^2 + k_2^2 + k_{-2}^2 + k_3^2 + k_{-3}^2 + 2(k_1(k_{-1} - k_{-2} + k_{-3}) + k_2(k_{-2} - k_{-3} + k_{-1}) + k_3(k_{-3} - k_{-1} + k_{-2})) - k_1k_2 - k_2k_3 - k_3k_1 - k_{-1}k_{-2} - k_{-2}k_{-3} - k_{-3}k_{-1}}}{2})$$

$$\lambda_3 = -\frac{1}{2}(k_1 + k_{-1} + k_2 + k_{-2} + k_3 + k_{-3} -$$

$$\frac{\sqrt{k_1^2 + k_{-1}^2 + k_2^2 + k_{-2}^2 + k_3^2 + k_{-3}^2 + 2(k_1(k_{-1} - k_{-2} + k_{-3}) + k_2(k_{-2} - k_{-3} + k_{-1}) + k_3(k_{-3} - k_{-1} + k_{-2})) - k_1k_2 - k_2k_3 - k_3k_1 - k_{-1}k_{-2} - k_{-2}k_{-3} - k_{-3}k_{-1}}}{2})$$

The eigenvectors are similar expressions, but even more lengthy. They are shown in the Maple worksheet. It is important to note that one of the eigenvalues is zero. From the solution in terms of the linear combinations of the concentrations (\underline{y}), then

$$y_1 = \exp(\lambda_1 t) y_{o,1} = y_{o,1}$$

This shows that the linear combination of concentrations given by y_1 remains constant in time. If we started with concentrations in that combination, the concentrations would not change. This combination of concentrations therefore represents the equilibrium composition of the mixture. This can also be seen by noting that the other two eigenvalues are negative, and therefore the components of the solution corresponding to them will go to zero at sufficiently large times, so that only the component corresponding to the zero eigenvalue will remain. When we have a network of reactions in which all of the reactions are reversible, like this one in the example, there will always be one zero eigenvalue in this analysis.

Properties of eigenvalues and eigenvectors:

We have seen that eigenvalues and eigenvectors play an essential role in defining the solution of systems of linear, first-order ODE's (linear initial value problems). Without launching into a long digression into matrix operations or linear algebra, it is worthwhile here to review the means of obtaining eigenvalues and eigenvectors, along with some key properties of eigenvalues and eigenvectors.

Eigenvalues are given by the roots of the *characteristic equation* of a square matrix. For an $n \times n$ matrix, $\underline{\underline{M}}$ this is a polynomial of the n^{th} degree that is obtained by evaluating:

$$\det(\underline{\underline{M}} - \lambda \underline{\underline{I}}) = 0$$

This polynomial has, in general, n solutions. If all elements of $\underline{\underline{M}}$ are real, then all of the coefficients of the characteristic polynomial will be real, and the eigenvalues will either be real or will come in complex conjugate pairs (i.e. if there is an eigenvalue $\lambda = a + ib$, there will be another eigenvalue $\lambda = a - ib$).

For each eigenvalue, the corresponding eigenvector is found by substituting the eigenvalue into the equation that defines eigenvalues and eigenvectors:

$$\underline{M}\underline{x}_i = \lambda_i \underline{x}_i \quad \text{or} \quad (\underline{M} - \lambda_i \underline{I})\underline{x}_i = 0$$

The matrix $(\underline{M} - \lambda_i \underline{I})$ is singular, and thus the eigenvector is only determined to within an arbitrary constant. That is, any scalar multiple of an eigenvector is also an eigenvector.

Other important properties of eigenvalues and eigenvectors:

- (1) The sum of all eigenvalues of a matrix is equal to the *trace* of the matrix, which is the sum of the diagonal elements.
- (2) Eigenvectors corresponding to different eigenvalues are linearly independent.
- (3) A matrix is singular if and only if it has a zero eigenvalue.
- (4) If \underline{x}_i is an eigenvector of \underline{M} corresponding to eigenvalue λ_i , and \underline{M} is invertible, then \underline{x}_i is also an eigenvector of \underline{M}^{-1} corresponding to its eigenvalue $1/\lambda_i$.
- (5) A matrix and its transpose have the same eigenvalues.
- (6) The eigenvalues of a triangular matrix are equal to its diagonal elements.
- (7) The product of the eigenvalues of a matrix equals the determinant of the matrix.
- (8) If \underline{x}_i is an eigenvector of \underline{M} corresponding to eigenvalue λ_i , then \underline{x}_i is also an eigenvector of $\underline{M} - c\underline{I}$ corresponding to its eigenvalue $\lambda_i - c$.

What you should be able to do after working through this set of lecture notes and the corresponding homework:

- (1) Write an arbitrary set of chemical reactions in matrix notation and in sum-product notation.
- (2) Write a set of rate equations in matrix form in terms of the stoichiometric matrix and reaction rates.
- (3) Determine the rank of a stoichiometric matrix and find a linearly independent set of reactions and a set of invariants of the system.
- (4) Write the set of linear first-order ordinary differential equations that are the rate equations for a network of first-order chemical reactions.
- (5) Solve this set of linear first-order ordinary differential equations in matrix form using the eigenvalues and eigenvectors of the matrix that multiplies the concentration vector to give the rates of change of the concentrations.
- (6) Find eigenvalues and eigenvectors both manually and using Mathematica, Maple, or a similar computer package.