5.6. Develop a computer program to implement Di Toro's efficient scheme for implementing feedforward first-order systems. Test your framework by using it to duplicate the results of Example 5.3.

5.7. Everyone's heard about the five Great Lakes described in this lecture. However, not everyone knows that there is a sixth lake in the system, Lake St. Clair, that is located on the river connecting Lakes Huron and Erie. By the standards of most other lakes, it's more than adequate ($V = 6.6\ \text{km}^3$, $A_s = 1114\ \text{km}^2$, $H = 5.9\ \text{m}$, $Q = 170.5\ \text{km}^3\ \text{yr}^{-1}$). However, in the context of the Great Lakes, it's at best a "Very Good Lake."

(*a*) Determine the responses of Lakes Huron, St. Clair, and Erie to an impulse flux of strontium (as described in Example 5.3) to Lake Huron. That is, compute the response as if the fallout fell only on Huron.

(*b*) Use the dimensionless analysis described at the end of the lecture to justify omitting Lake St. Clair from the Great Lakes.

LECTURE 6

Feedback Systems of Reactors

LECTURE OVERVIEW: I develop steady-state and time-variable solutions for coupled reactors with feedback. For the steady-state case, matrices are offered as a means to concisely represent systems of coupled reactors. I introduce the matrix inverse as a means to sort out the interactions between the reactors. For the time-variable case, the general solution is derived and an eigenvalue approach used to gain insight into the system's dynamics. In addition to systems of reactors the lecture also deals with modeling coupled reactions within a single reactor.

In the previous lecture we developed models for reactors in series. Now let's add feedback flows to these systems. Although this greatly increases the range of application of such models, it also complicates their solution. In fact, for all but the simplest systems (that is, two or three reactors), it means that computers are essential.

6.1 STEADY-STATE FOR TWO REACTORS

Mass balances for two CSTRs with feedback (Fig. 6.1) can be written as

$$V_1\frac{dc_1}{dt} = W_1 + Q_{01}c_0 - Q_{12}c_1 - k_1V_1c_1 + Q_{21}c_2 \tag{6.1}$$

$$V_2\frac{dc_2}{dt} = W_2 + Q_{12}c_1 - Q_{21}c_2 - Q_{23}c_2 - k_2V_2c_2 \tag{6.2}$$

At steady-state the terms can be collected and expressed as

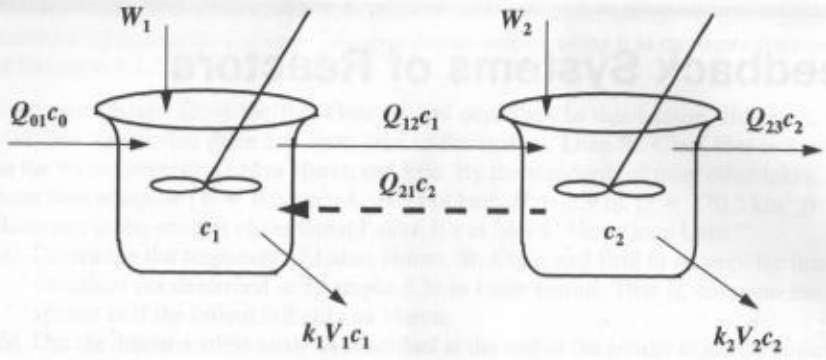


FIGURE 6.1
A system of reactors. The dashed arrow represents feedback.

$$a_{11}c_1 + a_{12}c_2 = W_1 \tag{6.3}$$

$$a_{21}c_1 + a_{22}c_2 = W_2 \tag{6.4}$$

where

$$a_{11} = Q_{12} + k_1V_1 \tag{6.5}$$

$$a_{12} = -Q_{21} \tag{6.6}$$

$$a_{21} = -Q_{12} \tag{6.7}$$

$$a_{22} = Q_{21} + Q_{23} + k_2V_2 \tag{6.8}$$

and the loading to the first reactor must be modified to include the inflow input

$$W_1 \leftarrow W_1 + Q_{01}c_0 \tag{6.9}$$

Thus we have two equations (6.3 and 6.4) with two unknowns. There are a variety of ways to obtain solutions. One convenient way, which is appropriate for small numbers of equations, is ***Cramer's rule.*** This rule states that each unknown in a system of linear algebraic equations may be expressed as a fraction of two determinants with the denominator as the system determinant. For example for a two equation system the denominator would be

$$D = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21} \tag{6.10}$$

The numerator is obtained from D by replacing the column of coefficients of the unknown in question by the constants W. For example c_1 would be computed as

$$c_1 = \frac{\begin{vmatrix} W_1 & a_{12} \\ W_2 & a_{22} \end{vmatrix}}{D} = \frac{a_{22}W_1 - a_{12}W_2}{a_{11}a_{22} - a_{12}a_{21}} \tag{6.11}$$

Similarly the second unknown could be determined as

$$c_2 = \frac{\begin{vmatrix} a_{11} & W_1 \\ a_{21} & W_2 \end{vmatrix}}{D} = \frac{a_{11}W_2 - a_{21}W_1}{a_{11}a_{22} - a_{12}a_{21}} \tag{6.12}$$

Algebraic manipulation can also be employed to express these results as

$$c_1 = \frac{1}{a_{11} - (a_{21}a_{12}/a_{22})}W_1 + \frac{1}{a_{21} - (a_{11}a_{22}/a_{12})}W_2 \tag{6.13}$$

$$c_2 = \frac{1}{a_{12} - (a_{11}a_{22}/a_{21})}W_1 + \frac{1}{a_{22} - (a_{21}a_{12}/a_{11})}W_2 \tag{6.14}$$

Thus we see that the concentrations are expressed in the format of Eq. 1.8. However, these solutions are considerably more complicated than Eq. 1.8. For Eqs. 6.13 and 6.14 the assimilation factors are now composites of a number of parameter groups. But due to the linearity of the original model (Eqs. 6.3 and 6.4), these results can provide great insight into how the system operates. In particular notice how each equation consists of two independent parts—one that is solely dependent on the first reactor's loading, W_1, and the other dependent on the loading to the second, W_2. This fact, which is a product of the model's linearity, allows us to separately evaluate the impact of the individual loadings.

Note that for more than three equations Cramer's rule becomes impractical because, as the number of equations increases, the determinants become too time-consuming to evaluate by hand (or by computers if they're calculated by expanding minors!). Consequently, as described next, more efficient methods are used.

6.2 SOLVING LARGE SYSTEMS OF REACTORS

The extension of the mass balance to more than two reactors is straightforward. For example for three coupled reactors with feedback, a set of three equations with three unknowns would be generated,

$$a_{11}c_1 + a_{12}c_2 + a_{13}c_3 = W_1 \tag{6.15}$$

$$a_{21}c_1 + a_{22}c_2 + a_{23}c_3 = W_2 \tag{6.16}$$

$$a_{31}c_1 + a_{32}c_2 + a_{33}c_3 = W_3 \tag{6.17}$$

where a's = constants that reflect the system parameters (that is, Q, V, k, etc.)
W's = constant loadings
c's = unknown concentrations

Note that the unknowns are all raised to the first power and are multiplied by a constant. Equations with these characteristics are called ***linear algebraic equations.***

In the previous section we used Cramer's rule to solve two equations with two unknowns. For more than two equations, this technique becomes computationally burdensome. Therefore in such cases, computers and numerical methods must be used. Several numerical methods are available for this purpose (see App. E and Chapra and Canale 1988 for details).

Aside from the mechanics of obtaining solutions, the representation and manipulation of large numbers of equations is difficult using simple algebra. For this reason the next section is devoted to matrix algebra.

6.2.1 Matrix Algebra

A ***matrix*** consists of a rectangular array of elements represented by a single symbol. For example

$$[A] = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \tag{6.18}$$

where $[A]$ is the shorthand notation for the entire matrix and a_{ij} designates an individual ***element*** of the matrix.

A horizontal set of elements is called a row and a vertical set is called a ***column.***[†] The first subscript i always designates the number of the row in which the element lies. The second subscript j designates the column. For example element a_{23} is in row two and column three.

A matrix can be characterized by its dimensions. It has n rows and m columns and is said to have a ***dimension*** of n by m (or $n \times m$). Such a matrix is commonly referred to as an ***n by m matrix***.

Matrices with column dimension $m = 1$ such as

$$\{B\} = \begin{Bmatrix} b_1 \\ b_2 \\ b_3 \end{Bmatrix} \tag{6.19}$$

are called ***column vectors.*** Note that for simplicity the second subscript of each element is dropped. Also it should be mentioned that it is often desirable to distinguish a column vector from other types of matrices. Consequently we use special brackets, { }, to enclose the values.

Matrices such as the one in Eq. 6.18, where $n = m$, are called ***square matrices.*** Square matrices are particularly important when solving sets of simultaneous linear equations. For such systems the number of equations (corresponding to the number of rows) and the number of unknowns (corresponding to the number of columns) must be equal for a unique solution to be possible. Consequently square matrices of coefficients are encountered when dealing with such systems.

There are a number of special types of square matrices. In the present context the most important is the ***identity matrix.*** For this case all elements are zero except for the diagonal that consists of ones. For the three by three case,

$$[I] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{6.20}$$

This matrix has properties similar to unity. Just as $a \times 1 = a$ in simple algebra, so also does

$$[A] \times [I] = [A] \tag{6.21}$$

[†]A simple mnemonic is provided by the horizontal "rows" of a theater and the vertical "columns" of a temple.

Matrix algebra follows rules in the same fashion as algebraic manipulations of simple variables. In the present context the two most important involve matrix multiplication and matrix inversion.

Matrix multiplication. The ***product*** of two matrices is represented as $[C] = [A][B]$, where the elements of $[C]$ are defined as

$$c_{ij} = \sum_{k=1}^{n} a_{ik} b_{kj} \tag{6.22}$$

where n = the column dimension of $[A]$ and the row dimension of $[B]$. That is, the c_{ij} element is obtained by adding the product of individual elements from the ith row of the first matrix, in this case $[A]$, and the jth column of the second matrix $[B]$. Box 6.1 illustrates a simple way to visualize matrix multiplication.

BOX 6.1. A Simple Method for Multiplying Two Matrices

Although Eq. 6.22 is well-suited for implementation on a computer, it is not the simplest means for visualizing the mechanics of multiplying two matrices. What follows gives more tangible expression to the operation.

Suppose that we want to multiply $[X]$ by $[Y]$ to yield $[Z]$:

$$[Z] = [X][Y] = \begin{bmatrix} 3 & 1 \\ 8 & 6 \\ 0 & 4 \end{bmatrix} \begin{bmatrix} 5 & 9 \\ 7 & 2 \end{bmatrix}$$

A simple way to visualize the computation of $[Z]$ is to raise $[Y]$, as in

$$\begin{bmatrix} 5 & 9 \\ 7 & 2 \end{bmatrix} \leftarrow [Y]$$

$$[X] \rightarrow \begin{bmatrix} 3 & 1 \\ 8 & 6 \\ 0 & 4 \end{bmatrix} \begin{bmatrix} \ ? \ \end{bmatrix} \leftarrow [Z]$$

Now the answer $[Z]$ can be computed in the space vacated by $[Y]$. This format has utility because it aligns the appropriate rows and columns that are to be multiplied. For example according to Eq. 6.22 the element z_{11} is obtained by multiplying the first row of $[X]$ by the first column of $[Y]$. This amounts to adding the product of x_{11} and y_{11} to the product of x_{12} and y_{21}, as in

$$\begin{bmatrix} \mathbf{5} & 9 \\ \mathbf{7} & 2 \end{bmatrix}$$

$$\downarrow$$

$$\begin{bmatrix} \mathbf{3} & \mathbf{1} \\ 8 & 6 \\ 0 & 4 \end{bmatrix} \rightarrow \begin{bmatrix} \mathbf{3 \times 5 + 1 \times 7 = 22} \\ \\ \end{bmatrix}$$

Thus z_{11} is equal to 22. Element z_{21} can be computed in a similar fashion, as in

$$\begin{bmatrix} 5 & 9 \\ 7 & 2 \end{bmatrix}$$
$$\downarrow$$
$$\begin{bmatrix} 3 & 1 \\ \mathbf{8} & \mathbf{6} \\ 0 & 4 \end{bmatrix} \rightarrow \begin{bmatrix} 22 \\ \mathbf{8 \times 5 + 6 \times 7 = 82} \end{bmatrix}$$

The computation can be continued in this way, following the alignment of the rows and columns, to yield the result

$$[Z] = \begin{bmatrix} 22 & 29 \\ 82 & 84 \\ 28 & 8 \end{bmatrix}$$

Note how this simple method makes it clear why it is impossible to multiply two matrices if the number of columns of the first matrix does not equal the number of rows in the second matrix. Also note how it demonstrates that the order of multiplication matters (that is, matrix multiplication is not commutative).

It should now be clear that matrices provide a succinct notation for representing simultaneous linear algebraic equations. For example Eqs. 6.15 to 6.17 can be expressed concisely as

$$[A]\{C\} = \{W\} \tag{6.23}$$

where the matrix $[A]$ contains the coefficients

$$[A] = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \tag{6.24}$$

the vector $\{C\}$ contains the unknowns

$$\{C\} = \begin{Bmatrix} c_1 \\ c_2 \\ c_3 \end{Bmatrix} \tag{6.25}$$

and the vector $\{W\}$ contains the right-hand-side constants or forcing functions,

$$\{W\} = \begin{Bmatrix} W_1 \\ W_2 \\ W_3 \end{Bmatrix} \tag{6.26}$$

At this point you should apply the rule for matrix multiplication to convince yourself that Eqs. 6.23 and 6.15 to 6.17 are equivalent.

Matrix inversion. Although multiplication is possible, matrix division is not a defined operation. However, if a matrix $[A]$ is square, there is usually another matrix $[A]^{-1}$ called the ***inverse*** of $[A]$ for which

$$[A][A]^{-1} = [A]^{-1}[A] = [I] \tag{6.27}$$

Thus the multiplication of a matrix by its inverse is analogous to division, in the sense that a number divided by itself is equal to 1. That is, multiplication of a matrix by its inverse leads to the identity matrix.

The inverse of a two-dimensional square matrix can be calculated simply, as in

$$[A]^{-1} = \frac{1}{a_{11}a_{22} - a_{12}a_{21}} \begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix} \tag{6.28}$$

Similar formulas for higher dimensional matrices are much more complicated. Consequently computer algorithms are usually used. One simple method involves standard computer solution algorithms such as Gauss elimination. For such cases each column j of the matrix inverse can be determined by using a unit vector (with a 1 in the jth row and 0 elsewhere) as the forcing-function vector (that is, the right-hand-side constants). Additional details can be found in App. E.

Once the inverse is obtained, a formal way to obtain a solution is to multiply each side of Eq. 6.23 by the inverse of $[A]$,

$$[A][A]^{-1}\{C\} = [A]^{-1}\{W\} \tag{6.29}$$

Because $[A]^{-1}[A]$ equals the identity matrix, the equation becomes

$$\{C\} = [A]^{-1}\{W\} \tag{6.30}$$

Therefore if we multiply the inverse of the coefficient matrix $[A]^{-1}$ by the matrix of constants $\{W\}$, we obtain the solution for the unknowns $\{C\}$. This is another example of how the inverse plays a role in matrix algebra similar to division. That is, just as $c = (1/a)W$ represents the steady-state solution for a single CSTR, Eq. 6.30 represents the solution for a system of CSTRs.

It should be noted that the matrix inverse is not a very efficient means to solve a system of equations. Thus other approaches, such as the elimination and iterative methods described in App. E, are used in numerical algorithms. However, as described next, the matrix inverse has great value in the engineering analysis of such systems.

6.3 STEADY-STATE SYSTEM RESPONSE MATRIX

Now that we have learned a little matrix algebra, we can explore its implications for steady-state solutions of coupled reactors with first-order kinetics. As described in the previous section, the matrix inverse can be used to obtain the solution for the steady-state case. In addition the terms in Eq. 6.30 have a definite physical interpretation. For example the elements of $\{C\}$ are the response of the system as reflected by the concentrations of the reactors. The right-hand-side vector $\{W\}$ contains the values of the system's stimuli or forcing functions—the loadings. Finally the matrix inverse $[A]^{-1}$ contains the parameters that express how the parts of the system are coupled and purge themselves of the pollutant. Consequently Eq. 6.30 might be reexpressed as

$$\{\text{Response}\} = [\text{interactions}]\{\text{stimuli}\} \tag{6.31}$$

In addition notice that Eq. 6.30 is the multidimensional manifestation of Eq. 1.8. This can be seen by applying the definition of matrix multiplication to Eq. 6.30. This gives

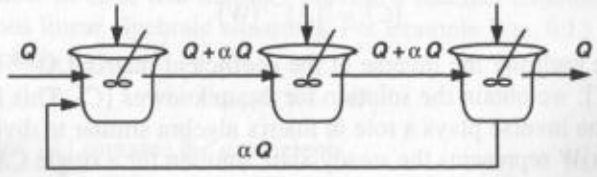
$$c_1 = a_{11}^{(-1)}W_1 + a_{12}^{(-1)}W_2 + a_{13}^{(-1)}W_3 \tag{6.32}$$

$$c_2 = a_{21}^{(-1)}W_1 + a_{22}^{(-1)}W_2 + a_{23}^{(-1)}W_3 \tag{6.33}$$

$$c_3 = a_{31}^{(-1)}W_1 + a_{32}^{(-1)}W_2 + a_{33}^{(-1)}W_3 \tag{6.34}$$

where $a_{ij}^{(-1)}$ denotes the element in the ith row and the jth column of the matrix inverse. Thus we find that the inverted matrix itself, aside from providing a solution, has extremely useful properties. That is, each of its elements represents the response of a single part of the system to a unit stimulus of any other part of the system.

EXAMPLE 6.1. STEADY-STATE SOLUTION FOR LAKES WITH FEEDBACK. Recall that in Example 5.1 we computed the steady-state distribution of a pollutant in three lakes connected in series. The same system is shown below, with the exception that we have recycled a fraction of the flow (α) from the third lake back to the first lake.



	1	2	3
Volume, 10^6 m^3	2	4	3
Mean depth, m	3	7	3
Surface area, 10^6 m^2	0.667	0.571	1.000
Loading, kg yr^{-1}	2000	4000	1000

FIGURE E6.1

(*a*) If $Q = 1 \times 10^6$ m^3 yr^{-1}, $\alpha = 0.5$, and the pollutant settles at a rate of 10 m yr^{-1}, calculate the concentration in each of the reactors.

(*b*) Use the matrix inverse to determine how much of the concentration in the third reactor is due to the loading to the second reactor.

(*c*) Determine the matrix inverse for the case where $\alpha = 0$.

Solution: (*a*) The steady-state mass balances for the three reactors can be written as

$$0 = W_1 - (Q + \alpha Q)c_1 - vA_1c_1 + \alpha Qc_3$$

$$0 = W_2 + (Q + \alpha Q)c_1 - (Q + \alpha Q)c_2 - vA_2c_2$$

$$0 = W_3 + (Q + \alpha Q)c_2 - (Q + \alpha Q)c_3 - vA_3c_3$$

Substituting the parameter values, the three simultaneous equations can be expressed in matrix form as

$$\begin{bmatrix} 8.17 \times 10^6 & 0 & -0.5 \times 10^6 \\ -1.5 \times 10^6 & 7.21 \times 10^6 & 0 \\ 0 & -1.5 \times 10^6 & 11.5 \times 10^6 \end{bmatrix} \begin{Bmatrix} c_1 \\ c_2 \\ c_3 \end{Bmatrix} = \begin{Bmatrix} 2 \times 10^9 \\ 4 \times 10^9 \\ 1 \times 10^9 \end{Bmatrix}$$

The matrix inverse can be determined as

$$\begin{bmatrix} 1.23 \times 10^{-7} & 1.11 \times 10^{-9} & 5.33 \times 10^{-9} \\ 2.55 \times 10^{-8} & 1.39 \times 10^{-7} & 1.11 \times 10^{-9} \\ 3.33 \times 10^{-9} & 1.81 \times 10^{-8} & 8.71 \times 10^{-8} \end{bmatrix}$$

which can be multiplied by $\{W\}$ to give

$$\begin{Bmatrix} c_1 \\ c_2 \\ c_3 \end{Bmatrix} = \begin{Bmatrix} 255 \\ 608 \\ 166 \end{Bmatrix}$$

(*b*) The effect of a load to segment two on the concentration of segment three can be based on $a_{32}^{(-1)} = 1.81 \times 10^{-8}$ μg L^{-1}/mg yr^{-1}. The effect of the 4×10^9 mg yr^{-1} load to segment two on the concentration of segment three can be calculated as

$$c_3 \text{ (due to loadings to reactor 2)} = 1.81 \times 10^{-8}(4 \times 10^9) = 72.5 \ \mu\text{g L}^{-1}$$

(*c*) For the case where $\alpha = 0$, the three simultaneous equations can be expressed in matrix form as

$$\begin{bmatrix} 7.67 \times 10^6 & 0 & 0 \\ -1 \times 10^6 & 6.71 \times 10^6 & 0 \\ 0 & -1 \times 10^6 & 11.0 \times 10^6 \end{bmatrix} \begin{Bmatrix} c_1 \\ c_2 \\ c_3 \end{Bmatrix} = \begin{Bmatrix} 2 \times 10^9 \\ 4 \times 10^9 \\ 1 \times 10^9 \end{Bmatrix}$$

The matrix inverse can be determined as

$$\begin{bmatrix} 1.30 \times 10^{-7} & 0 & 0 \\ 1.94 \times 10^{-8} & 1.49 \times 10^{-7} & 0 \\ 1.77 \times 10^{-9} & 1.35 \times 10^{-8} & 9.09 \times 10^{-8} \end{bmatrix}$$

Notice how the superdiagonal terms go to zero when feedback is omitted.

Before proceeding to time-variable solutions, we should comment a bit more on the structure of the matrix inverse. As depicted in Fig. 6.2, regions of the matrix

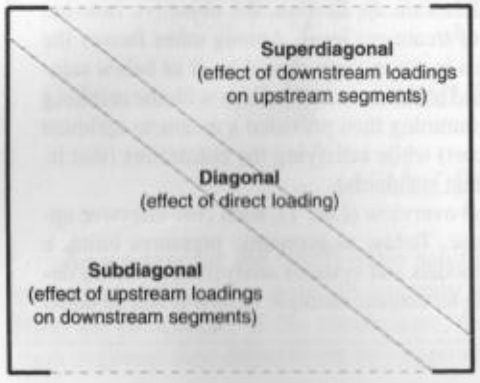


FIGURE 6.2
The elements of the matrix inverse $[A]^{-1}$ have a specific physical interpretation.

inverse $[A]^{-1}$ have a specific physical interpretation. Diagonal terms specify the response of the segments to direct loadings. The superdiagonal terms reflect the effect of downstream segments on upstream segments. The subdiagonal terms reflect the effect of upstream segments on downstream segments. Thus, as in part (*c*) of the previous example, a feedforward series system would have zero superdiagonal terms.

BOX 6.2. Input-Output Modeling and the Delaware Estuary Study

The steady-state system response matrix described in this lecture is an example of ***input-output modeling***. This approach was originally developed by W. W. Leontiff, the winner of the 1973 Nobel Prize for Economics. Leontiff derived linear systems of equations very similar to the ones in this lecture. However, rather than linking pollutant loadings with concentrations, he devised linear models that linked economic inputs (e.g., production of goods by sectors of the economy) with outputs (the consumption of the goods by other sectors).

The Delaware Estuary was the site of the first application of this approach in the water-quality domain. Located near Philadelphia, the Delaware Estuary is a critical water resource in the heavily populated Eastern United States. In the 1960s it was the site of the Delaware Estuary Comprehensive Study (FWPCA 1966), one of the first applications of computer-oriented water-quality modeling and systems analysis (Fig. 1.6). Despite having occurred over 30 yr ago, it remains one of the most comprehensive and innovative studies of its type (see Thomann 1972 for a nice summary).

Among the study's many contributions, the most relevant to water-quality modeling was the development of the control-volume approach described in this lecture. This framework (Thomann 1963) represented the doctoral research of the study's Technical Director, Bob Thomann, now a professor at Manhattan College. Along with the model, Dr. Thomann developed his own expression of the input-output approach in the form of the steady-state system response matrix.

In the present lectures I have emphasized how the matrix provides a concise way to link loadings with response. It should be noted that Dr. Thomann and his team (including Matt Sobal and Dave Marks, now professors at SUNY Stony Brook and at M.I.T., respectively) extended it well beyond this application. In particular they used the computer to develop treatment strategies that produced acceptable water quality at a minimum cost (Thomann and Sobal 1964). Specifically they employed a systems analysis approach known as ***linear programming***, designed to optimize an objective function subject to constraints. For the Delaware application, the objective function represented treatment cost as a function of treatment level. Among other factors the constraints reflected that the concentrations in the estuary should be at or below standards. The system response matrix was used to connect the loadings with the resulting concentrations in the estuary. Linear programming then provided a means to optimize the objective function (that is, minimize cost) while satisfying the constraints (that is, making sure the resulting concentrations met standards).

As already mentioned in our historical overview (Lec. 1), such cost-effective approaches have never found widespread use. Today, as economic pressures build, a revival may be at hand. The cause-effect models and systems analysis approaches developed 30 yr ago on the Delaware provide an elegant example of how it can be done.

6.4 TIME-VARIABLE RESPONSE FOR TWO REACTORS

Equations 6.1 and 6.2 (with no loads) can be written as

$$\frac{dc_1}{dt} = -\alpha_{11}c_1 + \alpha_{12}c_2 \tag{6.35}$$

$$\frac{dc_2}{dt} = \alpha_{21}c_1 - \alpha_{22}c_2 \tag{6.36}$$

where

$$\alpha_{11} = \frac{Q_{12}}{V_1} + k_1 \tag{6.37}$$

$$\alpha_{12} = \frac{Q_{21}}{V_1} \tag{6.38}$$

$$\alpha_{21} = \frac{Q_{12}}{V_2} \tag{6.39}$$

$$\alpha_{22} = \frac{Q_{23} + Q_{12}}{V_2} + k_2 \tag{6.40}$$

If $c_1 = c_{10}$ and $c_2 = c_{20}$, then the general solution can be developed as

$$c_1 = c_{1f}e^{-\lambda_f t} + c_{1s}e^{-\lambda_s t} \tag{6.41}$$

$$c_2 = c_{2f}e^{-\lambda_f t} + c_{2s}e^{-\lambda_s t} \tag{6.42}$$

where the λ's are eigenvalues that are defined as

$$\begin{matrix}\lambda_f \\ \lambda_s\end{matrix} = \frac{(\alpha_{11} + \alpha_{22}) \pm \sqrt{(\alpha_{11} + \alpha_{22})^2 - 4(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})}}{2} \tag{6.43}$$

and the coefficients are

$$c_{1f} = \frac{(\lambda_f - \alpha_{22})c_{10} - \alpha_{12}c_{20}}{\lambda_f - \lambda_s} \tag{6.44}$$

$$c_{1s} = \frac{\alpha_{12}c_{20} - (\lambda_s - \alpha_{22})c_{10}}{\lambda_f - \lambda_s} \tag{6.45}$$

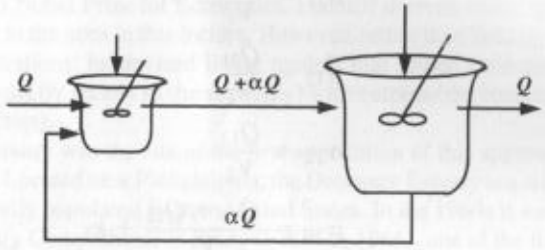
$$c_{2f} = \frac{-\alpha_{21}c_{10} + (\lambda_f - \alpha_{11})c_{20}}{\lambda_f - \lambda_s} \tag{6.46}$$

$$c_{2s} = \frac{-(\lambda_s - \alpha_{11})c_{20} + \alpha_{21}c_{10}}{\lambda_f - \lambda_s} \tag{6.47}$$

As we saw for the steady-state solution, the time-variable case is much more complicated than for a single completely mixed lake or for reactors in series. Aside from the complexity of the coefficients, the major difference is that the recovery of each segment now depends on two exponential decays.

The total recovery depends on the relative magnitudes of the eigenvalues. Note that λ_f will always be greater than λ_s. Consequently λ_f and λ_s are often referred to as the "fast" and the "slow" eigenvalues, respectively. This nomenclature derives from the rate at which they approach zero as time progresses. As in the following example, there are cases where the fast eigenvalue is much larger than the slow eigenvalue.

EXAMPLE 6.2. LAKES WITH FEEDBACK (TIME-VARIABLE). The following two lakes include feedback of a fraction of the flow (α) from the second lake back to the first lake:



	1	2
Volume, 10^6 m^3	0.2	10
Mean depth, m	4	20
Surface area, 10^6 m^2	0.05	0.5
Loading, kg yr^{-1}	2000	4000

FIGURE E6.2-1

Notice that for this case the second lake is much larger than the first.
(*a*) If $Q = 1 \times 10^6$ m^3 yr^{-1}, $\alpha = 0.5$, and the pollutant settles at a rate of 10 m yr^{-1}, calculate the steady-state concentration in each of the reactors.
(*b*) Using the concentrations calculated in (*a*) as initial conditions, determine the response of each lake if their loadings are terminated at $t = 0$.

Solution: (*a*) Using the same approach as in Example 6.1, the steady-state concentrations for the two reactors can be calculated as

$$\{c\} = \begin{Bmatrix} 1224.5 \\ 898 \end{Bmatrix}$$

(*b*) The temporal response can be determined by substituting the parameter values into Eqs. 6.41 and 6.42 to yield

$$c_1 = 981.24e^{-10.04t} + 243.25e^{-0.61t}$$

$$c_2 = -15.67e^{-10.04t} + 913.63e^{-0.61t}$$

The results are plotted in Fig. E6.2-2. As depicted, the concentration of the first reactor initially drops precipitously because of the dominance of its fast eigenvalue. After this initial drop its recovery slows down as its response becomes tied to the more sluggish recovery of the second reactor.

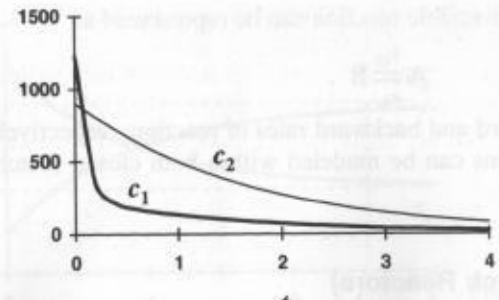


FIGURE E6.2-2

Although the foregoing analysis can be extended to many coupled reactors, most analyses of such systems are implemented numerically. We will review such techniques in the next lecture. Despite this fact the analytical, two-reactor case has general utility in water-quality analysis. This is because several important problem contexts can be modeled as two coupled reactors (Fig. 6.3). For example when we model toxic substances, a lake and its underlying sediments can be characterized in this way (Fig. 6.3*c*). In such cases the sediments typically respond much more slowly than the water. When loads are reduced, the lake's recovery will be retarded as sediment toxics seep back into the water. The eigenvalue approach outlined above can be useful in analyzing such cases.

6.5 REACTIONS WITH FEEDBACK

Aside from coupled reactors, the models developed in this lecture can be applied to reversible reactions occurring within a single reactor. For example, as previously

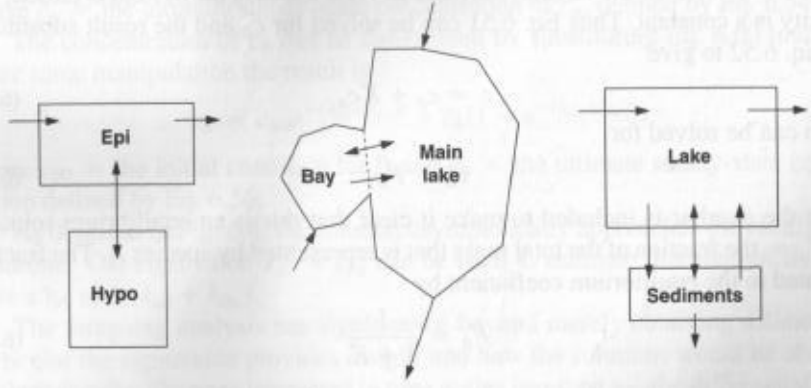


FIGURE 6.3
Three systems that can be characterized as a pair of coupled reactors. (*a*) The epilimnion (surface) and hypolimnion (bottom) of a stratified lake; (*b*) a lake with a major embayment; (*c*) a lake underlain by a sediment layer.

developed in Lec. 2, a simple reversible reaction can be represented as

$$A \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} B \tag{6.48}$$

where k_{ab} and k_{ba} = the forward and backward rates of reaction, respectively. We now examine how such reactions can be modeled within both closed (batch) and open (CSTR) reactors.

6.5.1 Closed Systems (Batch Reactors)

If the reactions are assumed to be first-order and to take place in a batch reactor, the following balances can be written:

$$\frac{dc_a}{dt} = -k_{ab}c_a + k_{ba}c_b \tag{6.49}$$

$$\frac{dc_b}{dt} = k_{ab}c_a - k_{ba}c_b \tag{6.50}$$

The steady-state solution of these equations can be obtained by setting the derivatives to zero and solving either equation for

$$\frac{c_b}{c_a} = \frac{k_{ab}}{k_{ba}} = K \tag{6.51}$$

where K = an equilibrium constant. Thus we arrive at the familiar result that, at equilibrium, the ratio of the products to the reactants of a chemical reaction will be constant.

To determine the magnitudes of c_a and c_b, we can define

$$c = c_a + c_b \tag{6.52}$$

where c = total mass of substances A and B. Now because the system is closed, this quantity is a constant. Thus Eq. 6.51 can be solved for c_b and the result substituted into Eq. 6.52 to give

$$c = c_a + Kc_a \tag{6.53}$$

which can be solved for

$$\overline{c}_a = F_a c \tag{6.54}$$

where the overbar is included to make it clear that this is an equilibrium solution, and F_a = the fraction of the total mass that is represented by species A. The fraction is related to the equilibrium coefficient by

$$F_a = \frac{1}{1 + K} \tag{6.55}$$

This result can then be substituted back into Eq. 6.52, which can be solved for

$$\overline{c}_b = F_b c \tag{6.56}$$

where F_b = the fraction of the total mass that is represented by species B,

$$F_b = 1 - F_a = \frac{K}{1 + K} \tag{6.57}$$

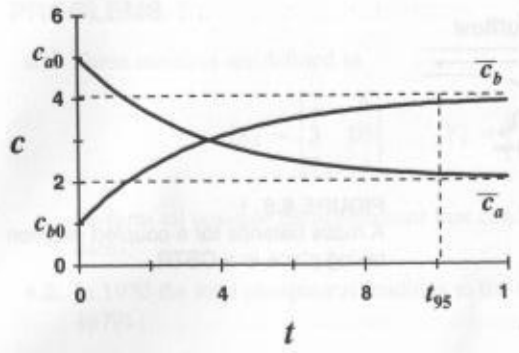


FIGURE 6.4
The progress of a reversible reaction within a batch reactor.

Thus, because we are at equilibrium, the concentrations of A and B are at fixed fractions of the total.

Next let us examine the time-variable solution. Although these equations can be solved using the methods described earlier in this lecture, an alternative approach involves solving Eq. 6.52 for c_b and substituting the result into Eq. 6.49 to give

$$\frac{dc_a}{dt} = -k_{ab}c_a + k_{ba}(c - c_a) \tag{6.58}$$

or collecting terms,

$$\frac{dc_a}{dt} + (k_{ab} + k_{ba})c_a = k_{ba}c \tag{6.59}$$

Thus the equation is a first-order ODE with a constant forcing function (recall Sec. 4.2). If $c = c_{a0}$ at $t = 0$, it can be solved for

$$c_a = c_{a0}e^{-(k_{ab}+k_{ba})t} + \overline{c}_a(1 - e^{-(k_{ab}+k_{ba})t}) \tag{6.60}$$

where $\overline{c}_a$ = the ultimate steady-state concentration of c_a, defined by Eq. 6.54.

The concentration of c_b can be determined by substituting Eq. 6.60 into 6.52. After some manipulation the result is

$$c_b = c_{b0}e^{-(k_{ab}+k_{ba})t} + \overline{c}_b(1 - e^{-(k_{ab}+k_{ba})t}) \tag{6.61}$$

where c_{b0} = the initial condition for B and $\overline{c}_b$ = the ultimate steady-state concentration defined by Eq. 6.56.

As depicted in Fig. 6.4, the solution asymptotically approaches the steady-state condition. The eigenvalue $k_{ab} + k_{ba}$ can be used to estimate that the reaction will have a t_{95} of $3/(k_{ab} + k_{ba})$.

The foregoing analysis has significance beyond merely obtaining solutions. In particular the eigenvalue provides insight into how the solutions would be obtained mathematically. If we are interested in time scales less than t_{95}, the differential equations would be solved directly to yield concentrations as a function of time. This is sometimes called a ***kinetic approach***, because we are interested in the time-variable or dynamic variations of the constituents. However, if we are not concerned with shorter time scales, the steady-state solutions (Eqs. 6.55 and 6.56) would be perfectly adequate. This is sometimes called an ***equilibrium approach***, because we are

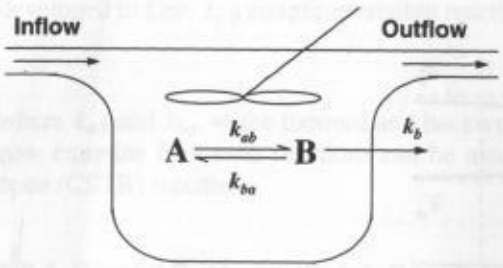


FIGURE 6.5
A mass balance for a coupled reaction taking place in a CSTR.

6.5.2 Open Systems (CSTRs)

Now let's explore how the foregoing analysis pertains to an open system. As in Fig. 6.5 suppose that the reversible reaction occurs in a CSTR. Both A and B are carried in and out of the reactor by flow. In addition assume that B is also subject to an additional reaction that removes it from the system. Mass balances can be written as

$$\frac{dc_a}{dt} = \frac{Q}{V}c_{a,\text{in}} - \frac{Q}{V}c_a - k_{ab}c_a + k_{ba}c_b \tag{6.62}$$

$$\frac{dc_b}{dt} = \frac{Q}{V}c_{b,\text{in}} - \frac{Q}{V}c_b + k_{ab}c_a - k_{ba}c_b - k_b c_b \tag{6.63}$$

These equations can be solved using the approaches described in earlier parts of this lecture. However, we will look at a special case. This relates to situations in which the coupling reaction rates k_{ab} and k_{ba} are much faster than the input-output or purging rates Q/V and k_b. For example if k_{ab} and k_{ba} were on the order of 1 hr^{-1} and the purging rates were 1 yr^{-1}, the coupling reactions would always be at a ***local equilibrium*** on an annual or even a daily time scale. In this case Di Toro (1976) has shown that Eqs. 6.62 and 6.63 can be added together to yield

$$\frac{dc}{dt} = \frac{Q}{V}c_{\text{in}} - \frac{Q}{V}c - k_b c_b \tag{6.64}$$

where c = total concentration = $c_a + c_b$ and c_{in} = total inflow concentration = $c_{a,\text{in}} + c_{b,\text{in}}$.

Notice that the terms representing the fast reactions were canceled by the addition of the equations. This is justified by the fact that if the reactions are at equilibrium, the terms $k_{ab}c_a$ and $k_{ba}c_b$ are equal and would cancel out.

Now at this point the mass balance, although simpler, cannot be solved because it is a single equation with two unknowns, c and c_b. However, the second can be eliminated by substituting Eq. 6.56 to give

$$\frac{dc}{dt} = \frac{Q}{V}c_{\text{in}} - \frac{Q}{V}c - k_b F_b c \tag{6.65}$$

Thus the original system of differential equations has been replaced by a single mass balance that can be solved for the total mass in the system as a function of time. Then at every time step, Eqs. 6.54 and 6.56 can be used to calculate the

PROBLEMS

6.1. Three matrices are defined as

$$[X] = \begin{bmatrix} 2 & 6 \\ 3 & 10 \\ 7 & 4 \end{bmatrix} \quad [Y] = \begin{bmatrix} 6 & 0 \\ 1 & 4 \end{bmatrix} \quad [Z] = \begin{bmatrix} 2 & 1 \\ 6 & 8 \end{bmatrix}$$

Perform all possible multiplications that can be computed between pairs of these matrices.

6.2. In 1970 the total phosphorus loadings to the Great Lakes were (Chapra and Sonzogni 1979)

	Units	Superior	Michigan	Huron	Erie	Ontario
W	tonnes yr^{-1}	4000	6950	4575	18,150	6650

(*a*) If total phosphorus settles at a rate of approximately 16 m yr^{-1}, calculate the steady-state concentration for each lake using the matrix inverse approach.
(*b*) Use the matrix inverse to determine how much of Lake Ontario's concentration is due to the loading to Lake Huron.
(*c*) Use the matrix inverse to determine how much Lake Ontario's concentration will change if Lake Erie's loading is reduced by 25% and Lake Huron's loading is halved.

6.3. Use Laplace transforms to solve Eqs. 6.35 and 6.36 for Eqs. 6.41 and 6.42.

6.4. As depicted in Fig. P6.4, a lake and its bottom segments can be modeled as two CSTRs with feedback.

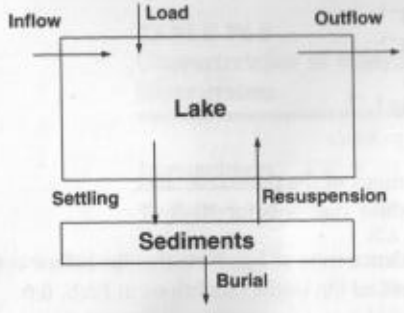


FIGURE P6.4

The following parameters are given:

Inflow = outflow = 20×10^6 m^3 yr^{-1}
Lake volume = 150×10^6 m^3
Settling velocity = 10 m yr^{-1}
Burial velocity = 2 mm yr^{-1}
Lake area = sediment area = 2.5×10^6 m^2
Sediment volume = 100×10^4 m^3
Resuspension velocity = 1 mm yr^{-1}

(*a*) If the lake receives a constant inflow concentration of 100 $\mu\text{g L}^{-1}$ and the pollutant does not react, but does settle, compute the steady-state concentration in the sediments and the water. Use the matrix inverse to determine the concentrations.
(*b*) If a sediment concentration of 100,000 $\mu\text{g L}^{-1}$ must be maintained, use the matrix

(*c*) Suppose that a spill of 20 kg of a contaminant occurs in the lake. Calculate the concentration in the lake and the sediments as a function of time in the following years.

6.5. Suppose that a spill of 5 kg of a pesticide takes place in the lake described in Prob. 6.4. Assume that 50% of the pesticide associates with solid matter and settles but does not volatilize (that is, it is not lost to the atmosphere). The other 50% is soluble and subject to volatilization (but not settling) that can be characterized by the first-order flux

$$J = v_v F_d c$$

where v_v = a volatilization mass-transfer coefficient of 0.01 m d^{-1} and F_d = the fraction of pesticide in dissolved form (in this case 0.5). Calculate the response of the system to the spill. When does the peak concentration occur in the sediments? Note that the lake is pesticide-free prior to the spill.

6.6. Suppose that the following first-order reactions take place in a batch reactor:

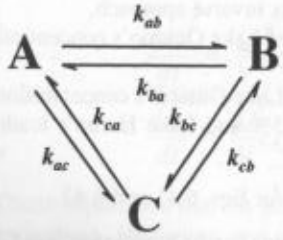


FIGURE P6.6

The following parameters and initial conditions apply:

$k_{ab} = 0.1$ d^{-1}	$k_{ba} = 0.2$ d^{-1}
$k_{bc} = 0.4$ d^{-1}	$k_{cb} = 0.5$ d^{-1}
$k_{ac} = 0.3$ s^{-1}	$k_{ca} = 0.6$ s^{-1}
$c_{a0} = 10$ mg L^{-1}	$c_{b0} = 20$ mg L^{-1}
$c_{c0} = 70$ mg L^{-1}	

(*a*) Calculate the steady-state concentrations of the three reactants.
(*b*) Calculate the concentrations of the three reactants for 10 d.

6.7. Repeat Prob. 6.6 for a CSTR with a residence time of 1 d. Note that the inflow concentrations of the three reactants are the same as the initial conditions in Prob. 6.6.

6.8. Figure P6.8 shows a simplified schematic of the Colorado River system, and characteristics of the impoundments are summarized in Table P6.8.
(*a*) Solve for the chloride concentration in each of the reservoirs.
(*b*) Determine the steady-state system response matrix.
(*c*) Use the result of part (*b*) to evaluate the new concentration in Lake Havasu if the loading to Lake Powell is halved.
(*d*) Suppose that global warming reduces all outflows by 20%. Recalculate the concentrations for this scenario.
(*e*) Calculate the effect on Lake Powell if 1 tonne (1000 kg) of a conservative contaminant is spilled into Flaming Gorge.
(*f*) Repeat part (*e*) but for a contaminant with a half-life of 2 yr.

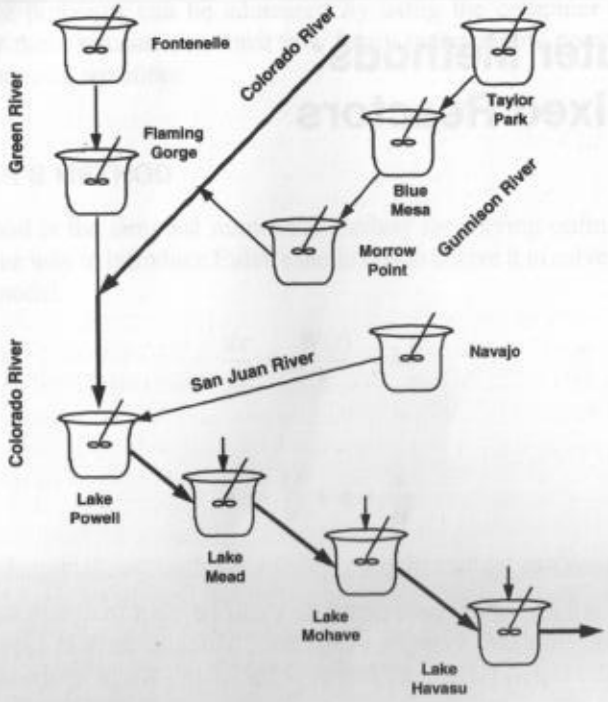


FIGURE P6.8
The Colorado River system.

TABLE P6.8
Characteristics of impoundments on the Colorado River system

Impoundment	Outflow (10^6 m^3 yr^{-1})	Volume (10^6 m^3)	Chloride loading (10^6 g yr^{-1})
Taylor Park	226	602	900
Blue Mesa	853	4,519	4,000
Morrow Point	914	851	400
Fontenelle	1,429	2,109	5,700
Flaming Gorge	1,518	19,581	20,000
Navajo	1,250	9,791	5,000
Powell	13,422	150,625	714,500
Mead	12,252	180,750	300,000
Mohave	12,377	12,050	102,000
Havasu	11,797	4,142	30,000