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1 Mathematical Modeling and Structured Programming

1.1 Elements of a Mathematical Model

At its heart, this book is about how to solve mathematical models of physical and engineering systems. In a mathematical model, we try to capture the essential chemistry and physics of a system. The resulting equations can be thought of as having the form

$$\mathcal{L}\mathbf{y} = \mathbf{f}(\mathbf{x}) \tag{1.1.1}$$

where $\mathcal{L}$ is a mathematical operator, $\mathbf{y}$ is a vector of unknowns, $\mathbf{x}$ is a vector of known quantities, and $\mathbf{f}$ is a vector of (forcing) functions. We have written out Eq. (1.1.1) in a rather general form without worrying about the precise nature of the operator $\mathcal{L}$, and we will discuss some specific details shortly. For the moment, let's consider the general solution to the problem.

In principle, "all" we need to do is determine the inverse of the operator, $\mathcal{L}^{-1}$. If we apply this inverse operator to the left and right sides of Eq. (1.1.1), then we have

$$\mathcal{L}^{-1}\mathcal{L}\mathbf{y} = \mathcal{L}^{-1}\mathbf{f}(\mathbf{x}) \tag{1.1.2}$$

By definition, the inverse operator "undoes" the operation $\mathcal{L}$, giving us back the unknowns that we are trying to compute,

$$\mathbf{y} = \mathcal{L}^{-1}\mathbf{f}(\mathbf{x}) \tag{1.1.3}$$

Figure 1.1 provides a schematic illustration of the inverse operator – it acts on the vector of inputs to produce the outputs. In the end, the goal of this book is to see how computers can compute $\mathcal{L}^{-1}$ for different types of problems and then apply these techniques to examples in chemical engineering.

While Eq. (1.1.3) is a generic result, it is only useful if (i) we understand the meaning of the various quantities appearing in Eq. (1.1.1) and (ii) we can actually figure out what the inverse operator is and how to apply it. Let us consider a few simple examples.

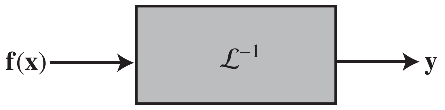

Figure 1.1 Idea behind a mathematical model. The inverse operator acts on the inputs to produce outputs.

Example 1.1 Explain the mathematical model

$$y + c = b \tag{1.1.4}$$

in the context of Eq. (1.1.1).

Solution

This is a simple example you probably saw in your first algebra class, although probably without the mathematical formalism we are using here. The operator adds the constant c to the value of a scalar y,

$$\mathcal{L}y = y + c \tag{1.1.5}$$

The forcing function is simply another constant, $f(x) = b$.

It should be apparent that the inverse operator, $\mathcal{L}^{-1}$, that solves Eq. (1.1.4) subtracts c,

$$\mathcal{L}^{-1}y = y - c \tag{1.1.6}$$

Applying the inverse operator to both sides of the equation yields the solution to the algebraic problem in Eq. (1.1.4),

$$y = b - c \tag{1.1.7}$$

Example 1.1 was a single, linear algebraic equation. In this case, the unknown vector $\mathbf{y}$ only contained one entry, which we denoted by the scalar y. Likewise, the forcing function contained a single scalar that we denoted as b. What if we have a system of algebraic equations?

Example 1.2 Explain the mathematical model

$$\mathbf{Ay} = \mathbf{b} \tag{1.1.8}$$

in the context of Eq. (1.1.1) where $\mathbf{A}$ is a square matrix.

Solution

The operator for a system equation is a matrix of constant coefficients, $\mathbf{A}$, that multiplies the unknowns $\mathbf{y}$. The forcing function is a vector of constants, $\mathbf{b}$.

You may recall Eq. (1.1.8) from your linear algebra classes in the form $\mathbf{Ax} = \mathbf{b}$, and we will use the latter form when we cover linear algebra. For the moment, we used the form in Eq. (1.1.8) to provide a direct correspondence with the notation in Eq. (1.1.1). Example 1.2 may also make it easier for you to see what we mean by the inverse operator $\mathcal{L}^{-1}$; for a system of linear algebraic systems, we need to compute the inverse of the

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matrix, $\mathbf{A}^{-1}$, and then left multiply it on both sides. If we apply this inverse operator to Eq. (1.1.8), we get

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{y} = \mathbf{A}^{-1}\mathbf{b} \tag{1.1.9}$$

Remembering that the product of a matrix and its inverse yields the identity matrix,

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{I} \tag{1.1.10}$$

and that multiplying a vector by the identity matrix just returns that vector,

$$\mathbf{I}\mathbf{y} = \mathbf{y} \tag{1.1.11}$$

we have the desired result

$$\mathbf{y} = \mathbf{A}^{-1}\mathbf{b} \tag{1.1.12}$$

In addition to helping us explain the concept of an operator, the solution of Eq. (1.1.8) is the heart of almost all numerical methods and thus one of the most important results of this chapter. We will spend considerable time in Chapter 2 on methods to solve linear algebraic equations.

The concept of an operator is more general than the algebraic examples we have considered so far. For example, differentiation is also a mathematical operation,

$$\mathcal{L} = \frac{d}{dx} \tag{1.1.13}$$

and its inverse is integration

$$\mathcal{L}^{-1} = \int \cdots dx \tag{1.1.14}$$

Differential equations form an important part of chemical engineering modeling and the subject of a large portion of this book, from Chapters 4 to 7.

Example 1.3 Explain the mathematical model

$$\frac{dy}{dx} = y \tag{1.1.15}$$

in the context of Eq. (1.1.1).

Solution

To have the correspondence with the definition of an operator, we should rewrite the equation as

$$\frac{dy}{dx} - y = 0 \tag{1.1.16}$$

The operator of this equation is differentiation with respect to x and subtraction of the unknown function. The forcing function is zero. Equations where the forcing function is zero are called *homogeneous equations.*

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The previous examples are linear problems, either linear algebraic equations or linear differential equations. While we will work with some linear problems in this book, for the most part to provide solvable problems to test out the numerical methods, many of the more interesting examples will be nonlinear problems. We can still use the formalism of an operator for nonlinear problems, but as the number and complexity of the equations increases, it becomes no longer possible to write out the operator in an explicit form. For example, consider the solution of the incompressible Navier–Stokes equations,

$$\nabla \cdot \mathbf{v} = 0 \tag{1.1.17}$$

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \eta \nabla^2 \mathbf{v} \tag{1.1.18}$$

for the fluid velocity vector $\mathbf{v}$, density ρ, and pressure p. In the latter, ∇ is the gradient operator and η is the fluid viscosity. The system of equations described by Eqs. (1.1.17) and (1.1.18) is very challenging to solve. Indeed, it is not even obvious how to write these equations in the standard operator form of Eq. (1.1.1), let alone determine an inverse operator!

1.2 Some Analytically Solvable Chemical Engineering Models

One of our goals in this book is to teach you how to numerically solve chemical engineering problems that do not have closed-form, analytical solutions. In order to motivate the following chapters, let's take a moment to consider a few problems that you may have seen in other chemical engineering classes. One reason these problems appeared in your other chemical engineering classes is that they can actually be solved analytically in a closed form. We will briefly review the solution methods for these problems too, since we will need their analytical solutions later in the book to validate the numerical methods. We will also highlight small changes to the problem, such as which parameters are the knowns and which are the unknowns, or whether or not the system is isothermal, that make the problem unsolvable by analytical methods. In this way, we hope to make it clear why you need numerical methods and point the way forward to some of the examples you will see in later chapters. Moreover, as the problems get increasingly complicated, the analytical solution becomes rather difficult. As a result, you may want to solve these later problems using numerical methods too, if for no other reason than to check your analytical solution with a particular numerical example.

1.2.1 Vapor–Liquid Equilibrium

A two-component system reaches two-phase equilibrium if the chemical potentials of the species in each phase are equal. For an ideal vapor/liquid system, this thermodynamic condition leads to the system of equations

$$x_1 P_1^{sat}(T) = y_1 P \tag{1.2.1}$$

$$(1 - x_1) P_2^{sat}(T) = (1 - y_1) P \tag{1.2.2}$$

where x_1 and y_1 are the mole fractions of species 1 in the liquid and vapor phases, respectively, P is the system pressure, and P_i^{sat} is the saturation pressure of species i, which depends only on temperature. There are four variables and only two equations, so we need to specify two variables and then we can solve for the other two.

If we pick the temperature and pressure as the known parameters (i.e. the quantities in the forcing function of the mathematical model), then the equilibrium conditions reduce to a system of two linear algebraic equations. This system can easily be solved by adding together the two equations

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} \tag{1.2.3}$$

and then using the equilibrium of species 1 to get the vapor composition,

$$y_1 = \frac{1 - P_2^{sat}/P}{1 - P_2^{sat}/P_1^{sat}} \tag{1.2.4}$$

This seems pretty easy! However, what happens if, instead of having two chemical species, we have a hundred species? For each species, we need to satisfy equilibrium

$$x_i P_i^{sat}(T) = y_i P, \quad i = 1, 2, \ldots, N \tag{1.2.5}$$

with the auxiliary equations

$$\sum_{i=1}^{N} x_i = 1 \tag{1.2.6}$$

and

$$\sum_{i=1}^{N} y_i = 1 \tag{1.2.7}$$

where N is the number of chemical species. (We will need to solve mass balance equations as well.) While each equation is linear in the mole fractions, solving a large system of equations by hand is not a trivial task. We will discuss the solution of large linear systems in Chapter 2, and revisit this particular example of multi-component flash in Section 2.7.

For linear systems, at least we know that we can find a solution (if one exists). For nonlinear problems, sometimes we can find a solution, sometimes not. For example, if we pick the liquid mole fraction and temperature as the known quantities, then we have a pair of nonlinear algebraic equations since y_1 and P multiply one another. However, this is still a solvable nonlinear problem because we can add the two equations to compute the system pressure,

$$P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat} \tag{1.2.8}$$

and then use the equilibrium of species 1 to get the vapor composition,

$$y_1 = \frac{x_1 P_1^{sat}}{x_1 P_1^{sat} + (1 - x_1) P_2^{sat}} \tag{1.2.9}$$

If we do not know the temperature, we again end up with a nonlinear equation because the saturation pressures are in general nonlinear functions of temperature. The so-called Antoine equation is a common empirical relationship between saturation pressure and temperature,

$$\log_{10} P_i^{sat} = A_i + \frac{B_i}{T + C_i} \tag{1.2.10}$$

where A_i, B_i, and C_i are constants for a particular chemical moiety. Let's assume that we know the partial pressures of each species (i.e., y_1 and P). Then we need to solve the equations

$$x_1 10^{A_1 + \frac{B_1}{T+C_1}} = y_1 P \tag{1.2.11}$$

$$(1 - x_1) 10^{A_2 + \frac{B_2}{T+C_2}} = (1 - y_1) P \tag{1.2.12}$$

There is no nice trick to solve for the temperature and liquid phase composition. At this point, we are forced to resort to the numerical methods that we will teach you in Chapter 3.

The situation only becomes more complicated when we drop the assumption of an ideal liquid phase, which then requires an activity coefficient γ_i, or the assumption of an ideal vapor phase, which leads to computing the fugacity. In the former case, our system of equations becomes

$$x_1 \gamma_1(T, x_1) P_1^{sat}(T) = y_1 P \tag{1.2.13}$$

$$(1 - x_1) \gamma_2(T, x_1) P_2^{sat}(T) = (1 - y_1) P \tag{1.2.14}$$

The nonlinearities here can be very complicated, since the activity coefficients depend on both temperature and composition. Moreover, the dependence of the activity coefficient on these parameters is often exponential, which is a very nonlinear coupling between the unknowns. These challenging non-ideal equilibrium calculations will be the subject of a case study in Section 3.10.

1.2.2 Batch Reactor with a Single Reactant

In a batch reactor, the reactants are fed to a closed system at time $t = 0$ and undergo a reaction. If we have a single reactant, say species A, that is consumed by the reaction in a constant volume system, then the mass balance on this species is

$$\frac{dc_A}{dt} = -r(c_A) \tag{1.2.15}$$

where $r(c_A)$ is the rate of consumption of species A per unit volume and c_A is the concentration of species A. In our model, this reaction rate depends on the concentration of A but no other parameters, such as temperature. In order to determine the concentration of species A, we also need to specify its initial concentration,

$$c_A(t = 0) = c_0 \tag{1.2.16}$$

These types of problems are called initial value problems and form the basis for Chapters 4 and 5.

Equation (1.2.15) is a separable, first-order differential equation. As a result, we can write its solution as

$$\int_{c_0}^{c_A(t)} \frac{dy}{r(y)} = -\int_0^t dx \tag{1.2.17}$$

In the latter, we have used x and y as dummy variables of integration. The second integral is trivial, so we can formally write the solution as

$$\int_{c_0}^{c_A(t)} \frac{dy}{r(y)} = -t \tag{1.2.18}$$

If we can compute the integral on the left-hand side and then solve the resulting algebraic equation for $c_A(t)$, then we know the concentration of species A.

Example 1.4 Determine the concentration profile for a batch reactor with the consumption rate $r(y) = k_1 y$.

Solution

For a first-order reaction, Eq. (1.2.18) becomes

$$\int_{c_0}^{c_A(t)} \frac{dy}{y} = -k_1 t \tag{1.2.19}$$

The integral gives back natural logarithms,

$$\int_{c_0}^{c_A(t)} \frac{dy}{y} = \ln \frac{c_A(t)}{c_0} \tag{1.2.20}$$

We thus have

$$c_A(t) = c_0 \exp(-k_1 t) \tag{1.2.21}$$

The first-order kinetics in Example 1.4 corresponds to a linear differential equation. One of the nice aspects of separable differential equations is that we can also solve nonlinear differential equations, provided that we can still calculate the integral.

Example 1.5 Determine the concentration profile for a batch reactor with the consumption rate $r(y) = k_2 y^2$.

Solution

For a second-order reaction, Eq. (1.2.18) becomes

$$\int_{c_0}^{c_A(t)} \frac{dy}{y^2} = -k_2 t \tag{1.2.22}$$

The integral now gives inverse powers of concentration,

$$\int_{c_0}^{c_A(t)} \frac{dy}{y^2} = -\left(\frac{1}{c_A(t)} - \frac{1}{c_0}\right) \tag{1.2.23}$$

We can then solve for the concentration,

$$c_A(t) = \frac{c_0}{1 + c_0 k_2 t} \tag{1.2.24}$$

What do we do when we cannot compute the integral for a separable equation? Aside from trying to find someone smarter than us to do the math (which is always a good idea!) or seeing if the integral is in a book somewhere, the numerical methods in Chapters 4 and 8 will allow us to construct approximate numerical solutions to otherwise unsolvable problems.

1.2.3 Batch Reactor with Three Species

The single reactant problem, which appears in the very start of a class on chemical kinetics, is a relatively simple mathematical model. Let's consider now a somewhat more challenging problem with multiple chemical species. From a pencil-and-paper standpoint, even the linear problem we will solve here is reasonably involved and we might just want to solve the problem numerically anyway.

As a concrete example, consider the reversible reaction A $\rightleftharpoons$ B and the irreversible reaction B → C in a constant volume batch reactor. The conservation equations for these three species are

$$\frac{dc_A}{dt} = -k_1 c_A + k_{-1} c_B \tag{1.2.25}$$

$$\frac{dc_B}{dt} = k_1 c_A - k_{-1} c_B - k_2 c_B \tag{1.2.26}$$

$$\frac{dc_C}{dt} = k_2 c_B \tag{1.2.27}$$

subject to initial conditions for each species. In the latter equations, the rate constants k_1 and k_{-1} refer to the forward and reverse reaction rates for the first reaction, while the rate constant k_2 is the forward reaction rate constant for the second reaction.

The problem actually only requires simultaneously solving Eqs. (1.2.25) and (1.2.26). Once we know $c_B(t)$, then we can use the separability of Eq. (1.2.27) to get

$$c_C = k_2 \int_0^t c_B(x)dx + c_C(0) \tag{1.2.28}$$

where x is the dummy variable of integration.

To compute the other two concentration profiles, we first rewrite the problem for species A and B in matrix form,

$$\frac{d}{dt}\begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} -k_1 & k_{-1} \\ k_1 & -(k_{-1}+k_2) \end{bmatrix}\begin{bmatrix} c_A \\ c_B \end{bmatrix} \tag{1.2.29}$$

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The formal solution of this problem is, under some technical assumptions that we will not discuss here, expressed in vector form as

$$\mathbf{c} = \sum_i a_i \mathbf{e}_i e^{\lambda_i t} \tag{1.2.30}$$

where a_i are constants of integration to be determined from the initial conditions, λ_i are the eigenvalues of the coefficient matrix in Eq. (1.2.29), and $\mathbf{e}_i$ are the corresponding eigenvectors.

In order to solve the problem, we need to remember how to compute eigenvalues and eigenvectors. (This review will certainly help you out in Chapter 5, where eigenvalues play a key role in our analysis of systems of initial value problems.) Given a matrix **A**, the eigenvalues are the solutions of

$$\det(\mathbf{A} - \lambda_i \mathbf{I}) = 0 \tag{1.2.31}$$

Once we know the eigenvalues, we can determine the eigenvectors as the non-zero vectors that satisfy

$$\mathbf{A}\mathbf{e}_i = \lambda_i \mathbf{e}_i \tag{1.2.32}$$

Example 1.6 Solve Eqs. (1.2.25)–(1.2.27) for the kinetic rate constants $k_1 = k_{-1} = 2$ and $k_2 = 3$ and the initial conditions $c_A(0) = 1$, $c_B(0) = 0$, and $c_C(0) = 0$.

Solution

For these kinetic constants, the coefficient matrix is

$$\begin{bmatrix} -k_1 & k_{-1} \\ k_1 & -(k_{-1} + k_2) \end{bmatrix} = \begin{bmatrix} -2 & 2 \\ 2 & -5 \end{bmatrix} \tag{1.2.33}$$

The eigenvalue equation is then

$$\det \begin{bmatrix} -2 - \lambda & 2 \\ 2 & -5 - \lambda \end{bmatrix} = 0 \tag{1.2.34}$$

Using the 2 × 2 determinant rule (see Appendix B), we have

$$\lambda^2 + 7\lambda + 6 = 0 \tag{1.2.35}$$

So the eigenvalues are $\lambda_1 = -1$ and $\lambda_2 = -6$.

We can then compute the corresponding eigenvectors. For λ_1, we need

$$\begin{bmatrix} -2 & 2 \\ 2 & -5 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \end{bmatrix} = - \begin{bmatrix} e_1 \\ e_2 \end{bmatrix} \tag{1.2.36}$$

Using the first equation we have

$$-2e_1 + 2e_2 = -e_1 \tag{1.2.37}$$

If we pick $e_1 = 1$ then we have

$$-2 + 2e_2 = -1 \tag{1.2.38}$$

so we get $e_2 = 1/2$. In math classes, you are often told to make normalized eigenvectors of unit length, i.e. $e_1^2 + e_2^2 = 1$. For solving ODEs, this is not important because we will adjust the length of the vector to satisfy the initial condition through the calculation of the coefficients a_i in Eq. (1.2.30). Indeed, since we would prefer to avoid dealing with fractions now, let's just multiply the eigenvector by 2 to have

$$\mathbf{e}_1 = \begin{bmatrix} 2 \\ 1 \end{bmatrix} \tag{1.2.39}$$

Note that our choice automatically satisfies the second of Eq. (1.2.36),

$$2e_1 - 5e_2 = -e_2 \tag{1.2.40}$$

For λ_2, we need to find e_1 and e_2 such that

$$\begin{bmatrix} -2 & 2 \\ 2 & -5 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \end{bmatrix} = -6 \begin{bmatrix} e_1 \\ e_2 \end{bmatrix} \tag{1.2.41}$$

Again using the first equation

$$-2e_1 + 2e_2 = -6e_1 \tag{1.2.42}$$

and the choice $e_1 = 1$ gives us $e_2 = -2$. So the second eigenvector is

$$\mathbf{e}_2 = \begin{bmatrix} 1 \\ -2 \end{bmatrix} \tag{1.2.43}$$

Using the eigenvalues and eigenvectors in the solution (1.2.30) gives us

$$\mathbf{c} = \begin{bmatrix} c_A \\ c_B \end{bmatrix} = a_1 \begin{bmatrix} 2 \\ 1 \end{bmatrix} e^{-t} + a_2 \begin{bmatrix} 1 \\ -2 \end{bmatrix} e^{-6t} \tag{1.2.44}$$

With the initial conditions $c_A(0) = 1$ and $c_B(0) = 0$, the coefficients are the solution to

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} = a_1 \begin{bmatrix} 2 \\ 1 \end{bmatrix} + a_2 \begin{bmatrix} 1 \\ -2 \end{bmatrix} \tag{1.2.45}$$

The solution to this problem is $a_1 = 2/5$ and $a_2 = 1/5$. As a result, the concentrations of species A and B are

$$\mathbf{c} = \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \frac{2}{5} \begin{bmatrix} 2 \\ 1 \end{bmatrix} e^{-t} + \frac{1}{5} \begin{bmatrix} 1 \\ -2 \end{bmatrix} e^{-6t} \tag{1.2.46}$$

If you prefer to have this written in component form,

$$c_A = \frac{4}{5} e^{-t} + \frac{1}{5} e^{-6t} \tag{1.2.47}$$

$$c_B = \frac{2}{5} e^{-t} - \frac{2}{5} e^{-6t} \tag{1.2.48}$$

We can now go back and compute c_C. Since its concentration is zero at $t = 0$, we have

$$c_C = 3 \int_0^t \left(\frac{2}{5} e^{-x} - \frac{2}{5} e^{-6x} \right) dx \tag{1.2.49}$$