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FORMULATION OF PHYSICOCHEMICAL PROBLEMS

1.1 INTRODUCTION

Modern science and engineering require high levels of qualitative logic before the act of precise problem formulation can occur. Thus, much is known about a physicochemical problem beforehand, derived from experience or experiment (i.e., empiricism). Most often, a theory evolves only after detailed observation of an event. This first step usually involves drawing a picture of the system to be studied.

The second step is the bringing together of all applicable physical and chemical information, conservation laws, and rate expressions. At this point, the engineer must make a series of critical decisions about the conversion of mental images to symbols, and at the same time, how detailed the model of a system must be. Here, one must classify the real purposes of the modeling effort. Is the model to be used only for explaining trends in the operation of an existing piece of equipment? Is the model to be used for predictive or design purposes? Do we want steady-state or transient response? The scope and depth of these early decisions will determine the ultimate complexity of the final mathematical description.

The third step requires the setting down of finite or differential volume elements, followed by writing the conservation laws. In the limit, as the differential elements shrink, then differential equations arise naturally. Next, the problem of boundary conditions must be addressed, and this aspect must be treated with considerable circumspection.

When the problem is fully posed in quantitative terms, an appropriate mathematical solution method is sought out, which finally relates dependent (responding) variables to one or more independent (changing) variables. The final result may be an elementary mathematical formula or a numerical solution portrayed as an array of numbers.

1.2 ILLUSTRATION OF THE FORMULATION PROCESS (COOLING OF FLUIDS)

We illustrate the principles outlined above and the hierarchy of model building by way of a concrete example: the cooling of a fluid flowing in a circular pipe. We start with the simplest possible model, adding complexity as the demands for precision increase. Often, the simple model will suffice for rough, qualitative purposes. However, certain economic constraints weigh heavily against overdesign, so predictions and designs based on the model may need be more precise. This section also illustrates the "need to know" principle, which acts as a catalyst to stimulate the garnering together of mathematical techniques. The problem posed in this section will appear repeatedly throughout the book, as more sophisticated techniques are applied to its complete solution.

1.2.1 Model I: Plug Flow

As suggested in the beginning, we first formulate a mental picture and then draw a sketch of the system. We bring together our thoughts for a simple plug flow model in Fig. 1.1*a*. One of the key assumptions here is *plug flow*, which means that the fluid velocity profile is plug shaped, in other words, uniform at all radial positions. This almost

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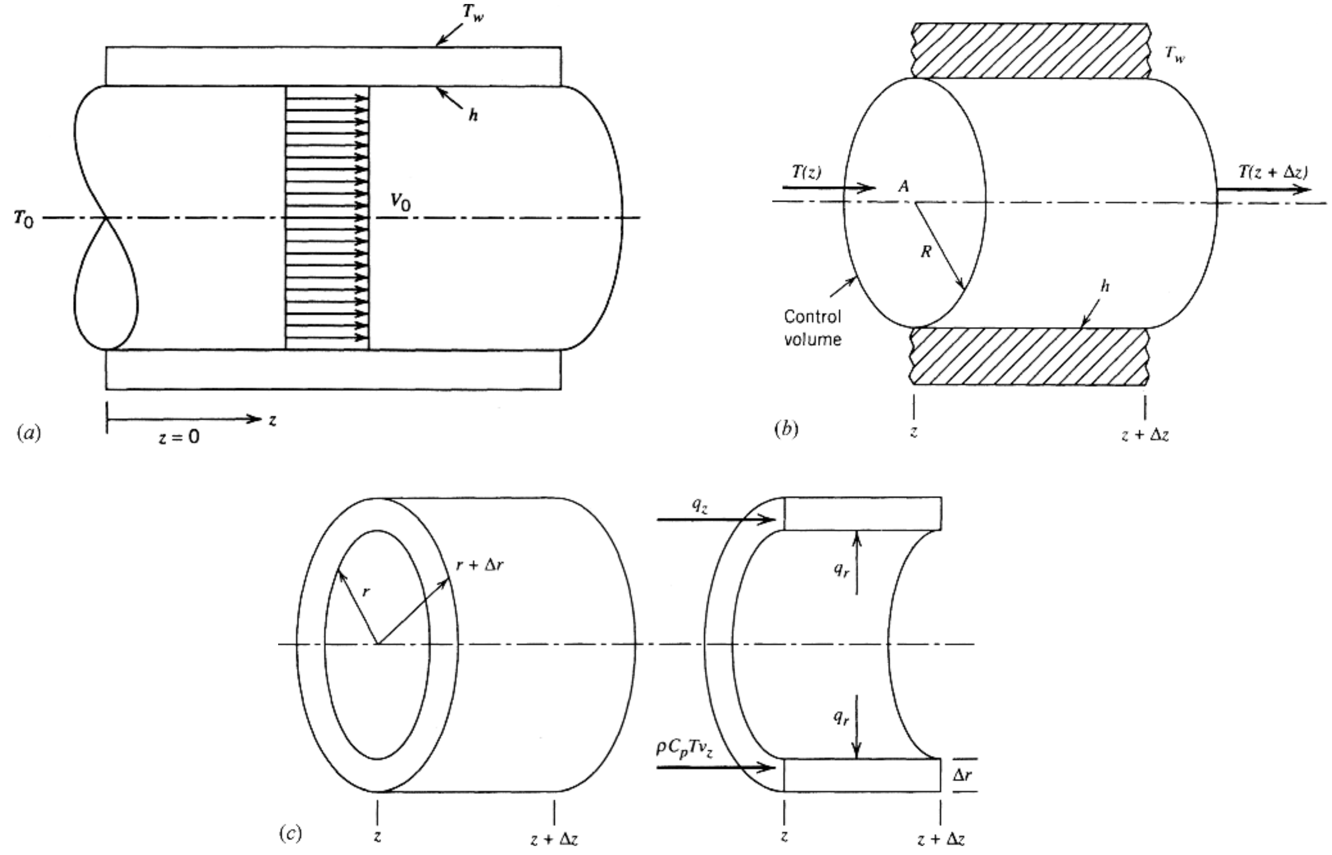


FIGURE 1.1 (*a*) Sketch of plug flow model formulation. (*b*) Elemental or control volume for plug flow model. (*c*) Control volume for Model II.

always implies turbulent fluid flow conditions, so that fluid elements are well mixed in the radial direction, hence the fluid temperature is fairly uniform in a plane normal to the flow field (i.e., the radial direction).

If the tube is not too long or the temperature difference is not too severe, then the physical properties of the fluid will not change much, so our second step is to express this and other assumptions as a list:

1. A steady-state solution is desired.
2. The physical properties (ρ, density; C_p, specific heat; k, thermal conductivity, etc.) of the fluid remain constant.
3. The wall temperature is constant and uniform (i.e., does not change in the z or r direction) at a value T_w.
4. The inlet temperature is constant and uniform (does not vary in r direction) at a value T_0, where $T_0 > T_w$.
5. The velocity profile is plug shaped or flat, hence it is uniform with respect to z or r.
6. The fluid is well mixed (highly turbulent), so the temperature is uniform in the radial direction.
7. Thermal conduction of heat along the axis is small relative to convection.

The third step is to sketch, and act upon, a differential volume element of the system (in this case, the flowing fluid) to be modeled. We illustrate this elemental volume in Fig. 1.1*b*, which is sometimes called the "control volume."

We act upon this elemental volume, which spans the whole of the tube cross section, by writing the general conservation law

$$\text{Rate in} - \text{rate out} + \text{rate of generation} \\ = \text{rate of accumulation} \qquad (1.1)$$

Since steady state is stipulated, the accumulation of heat is zero. Moreover, there are no chemical, nuclear, or electrical sources specified within the volume element, so heat generation is absent. The only way heat can be exchanged is through the perimeter of the element by way of the temperature difference between wall and fluid. The incremental rate of heat removal can be expressed as a positive quantity using Newton's law of cooling, that is,

$$\Delta Q = (2\pi R\Delta z)h\left[\overline{T}(z) - T_w\right] \tag{1.2}$$

As a convention, we shall express all such rate laws as positive quantities, invoking positive or negative signs as required when such expressions are introduced into the conservation law (Eq. 1.1). The contact area in this simple model is simply the perimeter of the element times its length.

The constant heat transfer coefficient is denoted by h. We have placed a bar over T to represent the average between $T(z)$ and $T(z+\Delta z)$

$$\overline{T}(z) \simeq \frac{T(z) + T(z+\Delta z)}{2} \tag{1.3}$$

In the limit, as $\Delta z \to 0$, we see

$$\lim_{\Delta z \to 0} \overline{T}(z) \to T(z) \tag{1.4}$$

Now, along the axis, heat can enter and leave the element only by convection (flow), so we can write the elemental form of Eq. 1.1 as

$$\underbrace{v_0 A\rho C_p T(z)}_{\text{Rate heat flow in}} - \underbrace{v_0 A\rho C_p T(z+\Delta z)}_{\text{Rate heat flow out}} - \underbrace{(2\pi R\Delta z)h(\overline{T} - T_w)}_{\text{Rate heat loss through wall}} = 0 \tag{1.5}$$

The first two terms are simply mass flow rate times local enthalpy, where the reference temperature for enthalpy is taken as zero. Had we used $C_p(T - T_{\text{ref}})$ for enthalpy, the term T_{ref} would be cancelled in the elemental balance. The last step is to invoke the fundamental lemma of calculus, which defines the act of differentiation

$$\lim_{\Delta z \to 0} \frac{T(z+\Delta z) - T(z)}{\Delta z} \to \frac{dT}{dz} \tag{1.6}$$

We rearrange the conservation law into the form required for taking limits, and then divide by Δz

$$-v_0 A\rho C_p \frac{T(z+\Delta z) - T(z)}{\Delta z} - (2\pi Rh)\left(\overline{T} - T_w\right) = 0 \tag{1.7}$$

Taking limits, one at a time, then yields the sought-after differential equation

$$v_0 A\rho C_p \frac{dT}{dz} + 2\pi Rh[T(z) - T_w] = 0 \tag{1.8}$$

where we have cancelled the negative signs.

Before solving this equation, it is good practice to group parameters into a single term (lumping parameters). For such elementary problems, it is convenient to lump parameters with the lowest order term as follows:

$$\frac{dT(z)}{dz} + \lambda[T(z) - T_w] = 0 \tag{1.9}$$

where

$$\lambda = 2\pi Rh/(v_0 A\rho C_p)$$

It is clear that λ must take units of reciprocal length.

As it stands, the above equation is classified as a linear, inhomogeneous equation of first order, which in general must be solved using the so-called integrating factor method, as we discuss later in Section 2.3.

Nonetheless, a little common sense will allow us to obtain a final solution without any new techniques. To do this, we remind ourselves that T_w is everywhere constant and that differentiation of a constant is always zero, so we can write

$$\frac{d(T(z) - T_w)}{dz} = \frac{dT(z)}{dz} \tag{1.10}$$

This suggests we define a new dependent variable, namely,

$$\theta = T(z) - T_w \tag{1.11}$$

hence Eq. 1.9 now reads simply

$$\frac{d\theta(z)}{dz} + \lambda\theta(z) = 0 \tag{1.12}$$

This can be integrated directly by separation of variables, so we rearrange to get

$$\frac{d\theta}{\theta} + \lambda dz = 0 \tag{1.13}$$

Integrating term by term yields

$$\ln\theta + \lambda z = \ln K \tag{1.14}$$

where $\ln K$ is any (arbitrary) constant of integration. Using logarithm properties, we can solve directly for θ

$$\theta = K\exp(-\lambda z) \tag{1.15}$$

It now becomes clear why we selected the form ln K as the arbitrary constant in Eq. 1.14.

All that remains is to find a suitable value for K. To do this, we recall the boundary condition denoted as T_0 in Fig. 1.1a, which in mathematical terms has the meaning

$$T(0) = T_0; \quad \text{or} \quad \theta(0) = T(0) - T_w = T_0 - T_w \tag{1.16}$$

Thus, when $z = 0$, $\theta(0)$ must take a value $T_0 - T_w$, so K must also take this value.

Our final result for computational purposes is

$$\frac{T(z) - T_w}{T_0 - T_w} = \exp\left(\frac{-2\pi R h z}{v_0 A \rho C_p}\right) \tag{1.17}$$

We note that all arguments of mathematical functions must be dimensionless, so the above result yields a dimensionless temperature

$$\frac{T(z) - T_w}{T_0 - T_w} = \psi \tag{1.18}$$

and a dimensionless length scale

$$\frac{2\pi R h z}{v_0 A \rho C_p} = \zeta \tag{1.19}$$

Thus, a problem with six parameters, two external conditions (T_0, T_w) and one each dependent and independent variable has been reduced to only two elementary (dimensionless) variables, connected as follows:

$$\psi = \exp(-\zeta) \tag{1.20}$$

1.2.2 Model II: Parabolic Velocity

In the development of Model I (plug flow), we took careful note that the assumptions used in this first model building exercise implied "turbulent flow" conditions, such a state being defined by the magnitude of the Reynolds number ($v_0 d/\nu$), which must always exceed 2100 for this model to be applicable. For slower flows, the velocity is no longer plug shaped, and in fact when $Re < 2100$, the shape is parabolic

$$v_z = 2v_0[1 - (r/R)^2] \tag{1.21}$$

where v_0 now denotes the average velocity and v_z denotes the locally varying value (Bird et al. 1960). Under such conditions, our earlier assumptions must be carefully reassessed; specifically, we will need to modify items 5–7 in the previous list:

5. The z-directed velocity profile is parabolic shaped and depends on the position r.
6. The fluid is not well mixed in the radial direction, so account must be taken of radial heat conduction.
7. Because convection is smaller, axial heat conduction may also be important.

These new physical characteristics cause us to redraw the elemental volume as shown in Fig. 1.1c. The control volume now takes the shape of a ring of thickness Δr and length Δz. Heat now crosses two surfaces, the annular area normal to fluid flow, and the area along the perimeter of the ring. We shall need to designate additional (vector) quantities to represent heat flux (rate per unit normal area) by molecular conduction:

$$q_r(r, z) = \text{molecular heat flux in radial direction} \tag{1.22}$$

$$q_z(r, z) = \text{molecular heat flux in axial direction} \tag{1.23}$$

The net rate of heat gain (or loss) by conduction is simply the flux times the appropriate area normal to the flux direction. The conservation law (Eq. 1.1) can now be written for the element shown in Fig. 1.1c.

$$\begin{aligned} &v_z(2\pi r\Delta r)\rho C_p T(z, r) - v_z(2\pi r\Delta r)\rho C_p T(z + \Delta z, r) \\ &\quad + (2\pi r\Delta r q_z)|_z - (2\pi r\Delta r q_z)|_{z+\Delta z} \\ &\quad + (2\pi r\Delta z q_r)|_r - (2\pi r\Delta z q_r)|_{r+\Delta r} = 0 \end{aligned} \tag{1.24}$$

The new notation is necessary, since we must deal with products of terms, either or both of which may be changing.

We rearrange this to a form appropriate for the fundamental lemma of calculus. However, since two position coordinates are now allowed to change, we must define the process of partial differentiation, for example,

$$\lim_{\Delta z \to 0} \frac{T(z + \Delta z, r) - T(z, r)}{\Delta z} = \left(\frac{\partial T}{\partial z}\right)_r \tag{1.25}$$

which, of course, implies holding r constant as denoted by subscript (we shall delete this notation henceforth). Thus, we divide Eq. 1.24 by $2\pi\Delta z\Delta r$ and rearrange to get

$$\begin{aligned} &-v_z \rho C_p r \frac{T(z + \Delta z, r) - T(z, r)}{\Delta z} - \frac{[rq_z]|_{z+\Delta z} - [rq_z]|_z}{\Delta z} \\ &\quad - \frac{[rq_r]|_{r+\Delta r} - [rq_r]|_r}{\Delta r} = 0 \end{aligned} \tag{1.26}$$

Taking limits, one at a time, then yields

$$-v_z \rho C_p r \frac{\partial T}{\partial z} - \frac{\partial (r q_z)}{\partial z} - \frac{\partial (r q_r)}{\partial r} = 0 \tag{1.27}$$

The derivative with respect to (wrt) z implies holding r constant, so r can be placed outside this term; thus, dividing by r and rearranging shows

$$-\frac{\partial q_z}{\partial z} - \frac{\partial}{r\partial r}(r q_r) = v_z \rho C_p \frac{\partial T}{\partial z} \tag{1.28}$$

At this point, the equation is insoluble since we have one equation and three unknowns (T, q_z, q_r). We need to know some additional rate law to connect fluxes q to temperature T. Therefore, it is now necessary to introduce the famous Fourier's law of heat conduction, the vector form of which states that heat flux is proportional to the gradient in temperature

$$q = -k \nabla T \tag{1.29}$$

and the two components of interest here are

$$q_r = -k \frac{\partial T}{\partial r}; \quad q_z = -k \frac{\partial T}{\partial z} \tag{1.30}$$

Inserting these two new equations into Eq. 1.28, along with the definition of v_z, yields finally a single equation, with one unknown $T(r,z)$

$$k\frac{\partial^2 T}{\partial z^2} + k\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = 2v_0 \rho C_p \left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial T}{\partial z} \tag{1.31}$$

The complexity of Model II has now exceeded our poor powers of solution, since we have much we need to know before attempting such second-order partial differential equations. We shall return to this problem occasionally as we learn new methods to effect a solution, and as new approximations become evident.

1.3 COMBINING RATE AND EQUILIBRIUM CONCEPTS (PACKED BED ADSORBER)

The occurrence of a rate process and a thermodynamic equilibrium state is common in chemical engineering models. Thus, certain parts of a whole system may respond so quickly that, for practical purposes, local equilibrium may be assumed. Such an assumption is an integral (but often unstated) part of the qualitative modeling exercise.

To illustrate the combination of rate and equilibrium principles, we next consider a widely used separation method, which is inherently unsteady, *packed bed adsorption*. We imagine a packed bed of finely granulated (porous) solid (e.g., charcoal) contacting a binary mixture, one component of which selectively adsorbs (physisorption) onto and within the solid material. The physical process of adsorption is so fast, relative to other slow steps (diffusion within the solid particle), that in and near the solid particles local equilibrium exists

$$q = KC^* \tag{1.32}$$

where q denotes the average composition of the solid phase, expressed as moles solute adsorbed per unit volume solid particle, and C^* denotes the solute composition (moles solute per unit volume fluid), which would exist at equilibrium. We suppose that a single film mass transport coefficient controls the transfer rate between flowing and immobile (solid) phase.

It is also possible to use the same model even when intraparticle diffusion is important (Rice 1982) by simply replacing the film coefficient with an "effective" coefficient. Thus, the model we derive can be made to have wide generality.

We illustrate a sketch of the physical system in Fig. 1.2. It is clear in the sketch that we shall again use the plug flow concept, so the fluid velocity profile is flat. If the stream to be processed is dilute in the adsorbable species (adsorbate), then heat effects are usually ignorable, so isothermal conditions will be taken. Finally, if the particles of solid are small, the axial diffusion effects, which are Fickian-like, can be ignored and the main mode of transport in the mobile fluid phase is by convection.

Interphase transport from the flowing fluid to immobile particles obeys a rate law, which is based on departure from the thermodynamic equilibrium state. Because the total interfacial area is not known precisely, it is common practice to define a volumetric transfer coefficient, which is the product $k_c a$, where a is the total interfacial area per unit

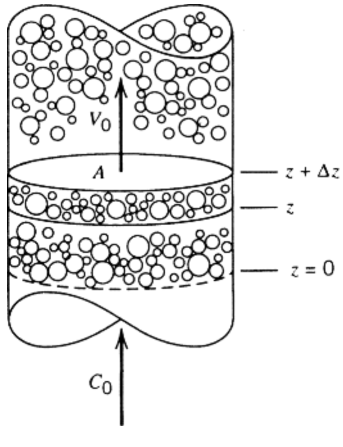


FIGURE 1.2 Packed bed adsorber.

volume of packed column. The incremental rate expression (moles/time) is then obtained by multiplying the volumetric transfer coefficient ($k_c a$) by the composition linear driving force and this times the incremental volume of the column ($A\Delta z$)

$$\Delta R = k_c a(C - C^*) \cdot A\Delta z \tag{1.33}$$

We apply the conservation law (Eq. 1.1) to the adsorbable solute contained in both phases as follows:

$$v_0 AC(z,\ t) - v_0 AC(z + \Delta z,\ t) = \varepsilon A\Delta z \frac{\partial C}{\partial t} + (1 - \varepsilon)A\Delta z \frac{\partial q}{\partial t} \tag{1.34}$$

where v_0 denotes superficial fluid velocity (velocity that would exist in an empty tube), ε denotes the fraction void (open) volume, hence $(1-\varepsilon)$ denotes the fractional volume taken up by the solid phase. Thus, ε is volume fraction between particles and is often called interstitial void volume; it is the volume fraction through which fluid is convected. The rate of accumulation has two possible sinks: accumulation in the fluid phase (C) and in the solid phase (q).

By dividing by $A\Delta z$, taking limits as before, we deduce that the overall balance for solute obeys

$$-v_0 \frac{\partial C}{\partial z} = \varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon)\frac{\partial q}{\partial t} \tag{1.35}$$

Similarly, we may make a solute balance on the immobile phase alone, using the rate law, Eq. 1.33, noting adsorption *removes* material from the flowing phase and *adds* it to the solid phase. Now, since the solid phase loses no material and generates none (assuming chemical reaction is absent), then the solid phase balance is

$$A(1 - \varepsilon)\Delta z \frac{\partial q}{\partial t} = k_c a(C - C^*)A\Delta z \tag{1.36}$$

which simply states that rate of accumulation equals rate of transfer to the solid. Dividing the elementary volume, $A\Delta z$, yields

$$(1 - \varepsilon)\frac{\partial q}{\partial t} = k_c a(C - C^*) \tag{1.37}$$

We note that as equilibrium is approached (as $C \to C^*$)

$$\frac{\partial q}{\partial t} \to 0$$

Such conditions correspond to "saturation," hence no further molar exchange occurs. When this happens to the whole bed, the bed must be "regenerated," for example, by passing a hot, inert fluid through the bed, thereby desorbing solute.

The model of the system is now composed of Eqs. 1.32, 1.35, and 1.37: There are three equations and three unknowns (C, C^*, q).

To make the system model more compact, we attempt to eliminate q, since $q = KC^*$; hence we have

$$v_0 \frac{\partial C}{\partial z} + \varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon)K \frac{\partial C^*}{\partial t} = 0 \tag{1.38}$$

$$(1 - \varepsilon)K \frac{\partial C^*}{\partial t} = k_c a(C - C^*) \tag{1.39}$$

The solution to this set of partial differential equations (PDEs) can be effected by suitable transform methods (e.g., the Laplace transform) for certain types of boundary and initial conditions (BC and IC). For the adsorption step, these are

$$q(z, 0) = 0 \text{ (initially clean solid)} \tag{1.40}$$

$$C(0, t) = C_0 \text{ (constant composition at bed entrance)} \tag{1.41}$$

The condition on q implies (cf. Eq. 1.32)

$$C^*(z, 0) = 0 \tag{1.42}$$

Finally, if the bed was indeed initially clean, as stated above, then it must also be true

$$C(z, 0) = 0 \text{ (initially clean interstitial fluid)} \tag{1.43}$$

We thus have three independent conditions (note, we could use either Eq. 1.40 or Eq. 1.42, since they are linearly dependent) corresponding to three derivatives:

$$\frac{\partial C^*}{\partial t}, \quad \frac{\partial C}{\partial t}, \quad \frac{\partial C}{\partial z}$$

As we demonstrate later, in Chapter 10, linear systems of equations can be solved exactly only when there exists one BC or IC for each order of a derivative. The above system is now properly posed, and will be solved as an example in Chapter 10 using Laplace transform.

1.4 BOUNDARY CONDITIONS AND SIGN CONVENTIONS

As we have seen in the previous sections, when time is an independent variable, the boundary condition is usually an initial condition, meaning we must specialize the state of the dependent variable at some time t_0 (usually $t_0 = 0$). For the steady state, we have seen that integrations of the applicable equations always produce arbitrary constants of integration. These integration constants must be evaluated, using stipulated boundary conditions to complete the model's solution.

For the physicochemical problems occurring in chemical engineering, most boundary or initial conditions are (or can be made to be) of the homogeneous type; *a condition or equation is taken to be homogeneous if, for example, it is satisfied by* y(x), *and is also satisfied by* λy(x), *where* λ *is an arbitrary constant*. The three classical types for such homogeneous boundary conditions at a point, say x_0, are the following:

$$\text{(i) } y(x) = 0 \quad @ \quad x = x_0$$

$$\text{(ii) } \frac{dy}{dx} = 0 \quad @ \quad x = x_0$$

$$\text{(iii) } \beta y + \frac{dy}{dx} = 0 \quad @ \quad x = x_0$$

Most often, the boundary values for a derived model are not homogeneous, but can be made to be so. For example, Model II in Section 1.2 portrays cooling of a flowing fluid in a tube. Something must be said about the fluid temperature at the solid wall boundary, which was specified to take a constant value T_w. This means all along the tube length, we can require

$$T(r, z) = T_w \quad @ \quad r = R, \quad \text{for all } z$$

As it stands, this does not match the condition for homogeneity. However, if we define a new variable θ

$$\theta = T(r, z) - T_w \tag{1.44}$$

then it is clear that the wall condition will become homogeneous, of type (i)

$$\theta(r, z) = 0 \quad @ \quad r = R, \quad \text{for all } z \tag{1.45}$$

When redefining variables in this way, one must be sure that the original defining equation is unchanged. Thus, since the derivative of a constant (T_w) is always zero, then Eq. 1.31 for the new dependent variable θ is easily seen to be unchanged

$$k\frac{\partial^2\theta}{\partial z^2} + k\left(\frac{\partial^2\theta}{\partial r^2} + \frac{1}{r}\frac{\partial\theta}{\partial r}\right) = 2v_0\rho C_p\left[1 - (r/R)^2\right]\frac{\partial\theta}{\partial z} \tag{1.46}$$

It often occurs that the heat (or mass) flux at a boundary is controlled by a heat (or mass) transfer coefficient, so for a circular tube the conduction flux is proportional to a temperature difference

$$q_r = -k\frac{\partial T}{\partial r} = U(T - T_c) \quad @ \quad r = R, \text{ for all } z; \qquad T_c = \text{constant} \tag{1.47}$$

Care must be taken to ensure that sign conventions are obeyed. In our cooling problem (Model II, Section 1.2), it is clear that

$$q_r > 0, \quad \frac{\partial T}{\partial r} \leq 0$$

so that $U(T - T_c)$ must be positive, which it is, since the coolant temperature $T_c < T(R, z)$.

This boundary condition also does not identify exactly with the type (iii) homogeneous condition given earlier. However, if we redefine the dependent variable to be $\theta = T - T_c$, then we have

$$\left(\frac{U}{k}\right)\theta + \frac{\partial\theta}{\partial r} = 0 \quad @ \quad r = R, \quad \text{for all } z \tag{1.48}$$

which is identical in form with the type (iii) homogeneous boundary condition when we note the equivalence: $\theta = y$, $U/k = \beta$, $r = x$, and $R = x_0$. It is also easy to see that the original convective diffusion Eq. 1.31 is unchanged when we replace T with θ. This is a useful property of linear equations.

Finally, we consider the type (ii) homogeneous boundary condition in physical terms. For the pipe flow problem, if we had stipulated that the tube wall was well insulated, then the heat flux at the wall is nil, so

$$q_r = -k\frac{\partial T}{\partial r} = 0 \quad @ \quad r = R, \quad \text{for all } z \tag{1.49}$$

This condition is of the homogeneous type (ii) without further modification.

Thus, we see that models for a fluid flowing in a circular pipe can sustain any one of the three possible homogeneous boundary conditions.

Sign conventions can be troublesome to students, especially when they encounter type (iii) boundary conditions. It is always wise to double-check to ensure that the sign of the left-hand side is the same as that of the right-hand side. Otherwise, negative transport coefficients will be produced, which is thermodynamically impossible. To guard against such inadvertent errors, it is useful to produce a sketch showing the qualitative shape of the expected profiles.

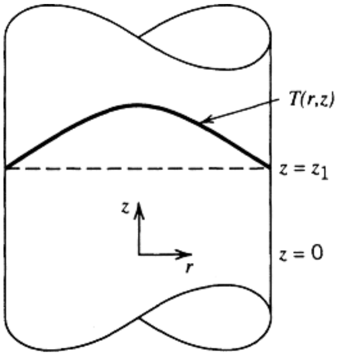


FIGURE 1.3 Expected temperature profile for cooling fluids in a pipe at an arbitrary position z_1.

In Fig. 1.3 we sketch the expected shape of temperature profile for a fluid being cooled in a pipe. The slope of temperature profile is such that $\partial T/\partial r \leq 0$. If we exclude the centerline ($r = 0$), where exactly $\partial T/\partial r = 0$ (the symmetry condition), then always $\partial T/\partial r < 0$. Now, since fluxes (which are vector quantities) are always positive when they move in the positive direction of the coordinate system, then it is clear why the negative sign appears in Fourier's law

$$q_r = -k\frac{\partial T}{\partial r} \tag{1.50}$$

Thus, since $\partial T/\partial r < 0$, then the product $-k\partial T/\partial r > 0$, so that flux $q_r > 0$. This convention thus ensures that heat moves down a temperature gradient, so transfer is always from hot to cold regions. For a heated tube, flux is always in the anti-*r* direction, hence it must be a negative quantity. Similar arguments hold for mass transfer where Fick's law is applicable, so that the radial component of flux in cylindrical coordinates would be

$$J_r = -D\frac{\partial C}{\partial r} \tag{1.51}$$

1.5 MODELS WITH MANY VARIABLES: VECTORS AND MATRICES

Large-scale industrial processes must deal with multicomponents and several phases in unit operations such as distillation, absorption, and catalytic cracking. The number of equations and variables needed to describe such processes are extensive and tedious to handle using traditional scalar mathematics. It is useful to introduce a body of mathematics that simplifies the representation of the many equations and variables in engineering processes; hence, we turn to vectors and matrices. This will allow the presentation of linear equations in a compact manner.

We will start with the definition of a matrix, with a vector being a special case of a matrix. Then we present a number of operations that may be used on matrices. Finally, we describe several methods for effecting the solution of linear equations.

1.6 MATRIX DEFINITION

A set of N linear algebraic equations with N unknowns, x_1, $x_2, \ldots, x_N$, may always be written in the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + \cdots + a_{1N}x_N &= b_1 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + \cdots + a_{2N}x_N &= b_2 \\ &\vdots \\ a_{N1}x_1 + a_{N2}x_2 + a_{N3}x_3 + \cdots + a_{NN}x_N &= b_N \end{aligned} \tag{1.52}$$

where x_i ($i = 1, 2, \ldots, N$) are unknown variables and b_i ($i = 1, 2, \ldots, N$) are the constants representing the nonhomogeneous terms. The coefficients a_{ij} ($i, j = 1, 2, \ldots, N$) are constant coefficients, with the index i representing the ith equation and the index j to correspond to the variable x_j.

N is the number of equations, and it can be any integer number, ranging from 1 to infinity. If N is a large number, it is time consuming to write those linear equations in the manner of Eq. 1.52. To facilitate the handling of large numbers of equations, the notation of matrices and vectors will become extremely useful. This will allow us to write sets of linear equations in a very compact form. Matrix algebra is then introduced that allows manipulation of these matrices, such as addition, subtraction, multiplication, and taking the inverse (similar to division for scalar numbers).

1.6.1 The Matrix

A *matrix* is a rectangular array of elements arranged in an orderly fashion with rows and columns. Each element is distinct and separate. The element of a matrix is denoted as a_{ij}, with the index i to represent the ith row and the index j to represent the jth column. The size of a matrix is denoted as $N \times M$, where N is the number of rows and M is the number of columns. We usually represent a matrix with a boldface capital letter, for example, $\mathbf{A}$, and the corresponding lowercase letter is used to represent its elements, for example, a_{ij}. The following equation shows the definition of a matrix $\mathbf{A}$ having N rows and M columns:

$$\mathbf{A} = \{a_{ij}; i = 1, 2, \ldots, N; j = 1, 2, \ldots, M\}$$
$$= \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1M} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2M} \\ & & & \cdots & . \\ a_{N1} & a_{N2} & a_{N3} & \cdots & a_{NM} \end{bmatrix} \quad (1.53)$$

where the bracket expression is the shorthand notation to describe both the element and the size of the matrix. The transpose of matrix **A** is denoted as $\mathbf{A}^{\mathbf{T}}$. It arises from the complete interchange of rows and columns of matrix **A**.

1.6.2 The Vector

A *vector* is a special case of a matrix. A vector can be put as a column vector or it can be put as a row vector. A column vector is a matrix having a size of $N \times 1$. For example, the following vector **b** is a column vector with size $N \times 1$:

$$\mathbf{b} = \{b_i; i = 1, 2, \ldots, N\} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \\ b_N \end{bmatrix} \quad (1.54)$$

where b_i is the element associated with the row i.

The row vector is a matrix having a size of $1 \times N$. For example, a row vector **d** is represented as

$$\mathbf{d} = \{d_i; i = 1, 2, \ldots, N\} = [d_1 \quad d_2 \quad d_3 \ldots d_N] \quad (1.55)$$

The transpose of this, $\mathbf{d}^{\mathbf{T}}$, is a column vector.

1.7 TYPES OF MATRICES

1.7.1 Square Matrix

A *square matrix* is a matrix that has the same number of rows and columns, that is, $\{a_{ij}; i, j = 1, 2, \ldots, N\}$. The elements a_{ii}, with $i = 1, 2, \ldots, N$, are called the major diagonal elements of the square matrix. The elements a_{N1}, $a_{N-1,2}$, to a_{1N} are called the minor diagonal elements.

1.7.2 Diagonal Matrix

A *diagonal matrix* is a square matrix having zero elements everywhere except on the major diagonal line. An identity matrix, denoted as **I**, is a diagonal matrix having unity major diagonal elements.

1.7.3 Triangular Matrix

A *triangular matrix* is a matrix having all elements on one side of the major diagonal line to be zero. An upper tridiagonal matrix **U** has all zero elements below the major diagonal line, and a lower tridiagonal matrix **L** has all zero elements above the diagonal line. The following equation shows upper and lower tridiagonal matrices having a size 3×3:

$$\mathbf{U} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & 0 & a_{33} \end{bmatrix}; \quad \mathbf{L} = \begin{bmatrix} a_{11} & 0 & 0 \\ a_{21} & a_{22} & 0 \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad (1.56)$$

1.7.4 Tridiagonal Matrix

A *tridiagonal matrix* is a matrix in which all elements that are not on the major diagonal line and two diagonals surrounding the major diagonal line are zero. The following equation shows a typical tridiagonal matrix of size 4×4

$$\mathbf{T} = \begin{bmatrix} a_{11} & a_{12} & 0 & 0 \\ a_{21} & a_{22} & a_{23} & 0 \\ 0 & a_{32} & a_{33} & a_{34} \\ 0 & 0 & a_{43} & a_{44} \end{bmatrix} \quad (1.57)$$

The tridiagonal matrix is encountered quite regularly when solving differential equations using the finite difference method (see Chapter 12).

1.7.5 Symmetric Matrix

The transpose of a $N \times M$ matrix **A** is a matrix $\mathbf{A}^T$ having a size of $M \times N$, with the element a_{ij}^T defined as

$$a_{ij}^T = a_{ji} \quad (1.58)$$

that is, the position of a row and a column is interchanged.

A symmetric square matrix has identical elements on either side of the major diagonal line, that is, $a_{ji} = a_{ij}$. This means $\mathbf{A}^T = \mathbf{A}$.

1.7.6 Sparse Matrix

A *sparse matrix* is a matrix in which most elements are zero. Many matrices encountered in solving engineering systems are sparse matrices.

1.7.7 Diagonally Dominant Matrix

A *diagonally dominant matrix* is a matrix such that the absolute value of the diagonal term is larger than the sum of the absolute values of other elements in the same row, with the diagonal term larger than the corresponding sum for at least one row; that is,

$$|a_{ii}| \geq \sum_{\substack{j=1 \\ j\neq i}}^{N} |a_{ij}| \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.59}$$

with

$$|a_{ii}| > \sum_{\substack{j=1 \\ j\neq i}}^{N} |a_{ij}| \tag{1.60}$$

for at least one row.

This condition of diagonal dominant matrix is required in the solution of a set of linear equations using iterative methods, details of which are given in Section 1.11.

1.8 MATRIX ALGEBRA

Just as in scalar operations, where we have addition, subtraction, multiplication, and division, we also have addition, subtraction, multiplication, and inverse (playing the role of division) on matrices, but there are a few restrictions in matrix algebra before these operations can be carried out.

1.8.1 Addition and Subtraction

These two operations can be carried out only when the sizes of the two matrices are the same. The operations are shown as follows.

$$\mathbf{A} + \mathbf{B} = \{a_{ij}\} + \{b_{ij}\} = \{c_{ij} = a_{ij} + b_{ij}\} = \mathbf{C} \tag{1.61}$$

$$\mathbf{A} - \mathbf{B} = \{a_{ij}\} - \{b_{ij}\} = \{c_{ij} = a_{ij} - b_{ij}\} = \mathbf{C} \tag{1.62}$$

Operations cannot be carried out on unequal size matrices.

Addition of equal size matrices is associative and commutative; that is,

$$\mathbf{A} + (\mathbf{B} + \mathbf{C}) = (\mathbf{A} + \mathbf{B}) + \mathbf{C} \tag{1.63}$$

$$\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A} \tag{1.64}$$

1.8.2 Multiplication

This operation involves the multiplication of the row elements of the first matrix to the column elements of the second matrix and the summation of the resulting products. Because of this procedure of multiplication, the number of columns of the first matrix, **A**, must be the same as the number of rows of the second matrix, **B**. Two matrices that satisfy this criterion are called conformable in the order of **A B**. If the matrix **A** has a size $N \times R$ and **B** has a size $R \times M$, the resulting product $\mathbf{C} = \mathbf{A} \cdot \mathbf{B}$ will have a size of $N \times M$, and the elements c_{ij} are defined as

$$c_{ij} = \sum_{r=1}^{R} a_{ir} b_{rj}; i = 1, 2, \ldots, N; j = 1, 2, \ldots, M \tag{1.65}$$

Matrices not conformable cannot be multiplied, and it is obvious that square matrices are conformable in any order.

Conformable matrices are associative on multiplication; that is,

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C} \tag{1.66}$$

but square matrices are generally not commutative on multiplication, that is,

$$\mathbf{AB} \neq \mathbf{BA} \tag{1.67}$$

Matrices **A**, **B**, and **C** are distributive if **B** and **C** have the same size and if **A** is conformable to **B** and **C**, then we have

$$\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC} \tag{1.68}$$

Multiplication of a matrix **A** with a scalar β is a new matrix **B** with the element $b_{ij} = \beta a_{ij}$.

1.8.3 Inverse

The inverse in matrix algebra plays a similar role to division in scalar division. The inverse is defined as follows:

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{I} \tag{1.69}$$

where $\mathbf{A}^{-1}$ is called the inverse of **A**, and **I** is the identity matrix. Matrix inverses commute on multiplication, that is,

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{I} = \mathbf{A}^{-1}\mathbf{A} \tag{1.70}$$

If we have the equation,

$$\mathbf{AB} = \mathbf{C} \tag{1.71}$$

where **A**, **B**, and **C** are square matrices, multiply the LHS and RHS of Eq. 1.71 by $\mathbf{A}^{-1}$ and we will get

$$\mathbf{A}^{-1}(\mathbf{AB}) = \mathbf{A}^{-1}\mathbf{C} \tag{1.72}$$

But since the multiplication is associative, the above equation will become

$$(\mathbf{A}^{-1}\mathbf{A})\mathbf{B} = \mathbf{B} = \mathbf{A}^{-1}\mathbf{C} \tag{1.73}$$

as $\mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$ and $\mathbf{IB} = \mathbf{B}$.

The analytical technique according to the Gauss–Jordan procedure for obtaining the inverse will be dealt with later.

1.8.4 Matrix Decomposition or Factorization

A given matrix **A** can be represented as a product of two conformable matrices **B** and **C**. This representation is not unique, as there are infinite combinations of **B** and **C** that can yield the same matrix **A**. Of particular usefulness is the decomposition of a square matrix **A** into lower and upper triangular matrices, shown as follows.

$$\mathbf{A} = \mathbf{LU} \tag{1.74}$$

This is usually called the *LU* decomposition and is useful in solving a set of linear algebraic equations.

1.9 USEFUL ROW OPERATIONS

A set of linear algebraic equations of the type in Eq. 1.52 can be readily put into vector–matrix format as

$$\mathbf{Ax} = \mathbf{b} \tag{1.75}$$

where

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1N} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2N} \\ & & & \cdots & . \\ a_{N1} & a_{N2} & a_{N3} & \cdots & a_{NN} \end{bmatrix}; \quad \mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{bmatrix}; \quad \mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_N \end{bmatrix} \tag{1.76}$$

Equation 1.76 can also be written in the component form as

$$\sum_{j=1}^{N} a_{ij}x_j = b_i; \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.77}$$

which is basically the equation of the row i.

There are a number of row operations that can be carried out and they do not affect the values of the final solutions **x**.

1.9.1 Scaling

Any row can be multiplied by a scalar, the process of which is called scaling. For example, the row i of Eq. 1.77 can be multiplied by a constant α as

$$\sum_{j=1}^{N} \alpha a_{ij}x_j = \alpha b_i \tag{1.78}$$

1.9.2 Pivoting

Any row can be interchanged with another row. This process is called pivoting. The main purpose of this operation is to create a new matrix that has dominant diagonal terms, which is important in solving linear equations.

1.9.3 Elimination

Any row can be replaced by a weighted linear combination of that row with any other row. This process is carried out on the row i with the purpose of eliminating one or more variables from that equation. For example, if we have the following two linear equations:

$$\begin{aligned} x_1 + x_2 &= 2 \\ 3x_1 + 2x_2 &= 5 \end{aligned} \tag{1.79}$$

Let us now modify the row 2; that is, equation number 2. We multiply the first row by (3) and then subtract the second row from this to create a new second row; hence we have

$$\begin{aligned} x_1 + x_2 &= 2 \\ 0x_1 + x_2 &= 1 \end{aligned} \tag{1.80}$$

We see that x_1 has been eliminated from the new second row, from which it is seen that $x_2 = 1$ and hence from the first row $x_1 = 1$. This process is called elimination. This is exactly the process used in the Gauss elimination scheme to search for the solution of a given set of linear algebraic equations, which will be dealt with in the next section.

There are a number of methods available to solve for the solution of a given set of linear algebraic equations. One class is the direct method (i.e., requires no iteration) and the other is the iterative method, which requires iteration as the name indicates. For the second class of method, an initial guess must be provided. We will first discuss the direct methods in Section 1.10 and the iterative methods will be dealt with in Section 1.11. The iterative methods are preferable when the number of equations to be solved is large, the coefficient matrix is sparse, and the matrix is diagonally dominant (Eqs. 1.59 and 1.60).

1.10 DIRECT ELIMINATION METHODS

1.10.1 Basic Procedure

The elimination method basically involves the elimination of variables in such a way that the final equation will involve only one variable. The procedure for a set of N equations is as follows. First, from one equation solve for x_1 as a function of other variables, $x_2, x_3, \ldots, x_N$. Substitute this x_1 into the remaining $N-1$ equations to obtain a new set of $N-1$ equations with $N-1$ unknowns, $x_2, x_3, \ldots, x_N$. Next, using one of the equations in the new set, solve for x_2 as a function of other variables, $x_3, x_4, \ldots, x_N$, and then substitute this x_2 into the remaining $N-2$ equations to obtain a new set of $N-2$ equations in terms of $N-2$ unknown variables. Repeat the procedure until you end up with only one equation with one unknown, x_N, from which we can readily solve for x_N. Knowing x_N, we can use it in the last equation in which x_{N-1} was written in terms of x_N. Repeat the same procedure to find x_1. The process of going backward to find solutions is called back substitution.

Let us demonstrate this elimination method with the following set of three linear equations:

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = b_1 \tag{1.81}$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = b_2 \tag{1.82}$$

$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 = b_3 \tag{1.83}$$

Assuming a_{11} is not zero, we solve Eq. 1.81 for x_1 in terms of x_2 and x_3 and we have

$$x_1 = \frac{b_1 - a_{12}x_2 - a_{13}x_3}{a_{11}} \tag{1.84}$$

Substitute this x_1 into Eqs. 1.82 and 1.83 to eliminate x_1 from the remaining two equations, and we have

$$a'_{22}x_2 + a'_{23}x_3 = b'_2 \tag{1.85}$$

$$a'_{32}x_2 + a'_{33}x_3 = b'_3 \tag{1.86}$$

where

$$a'_{ij} = a_{ij} - \frac{a_{i1}}{a_{11}}a_{1j}; \quad b'_i = b_i - \frac{a_{i1}}{a_{11}}b_1 \quad \text{for} \quad i,j = 2,3 \tag{1.87}$$

Next, we solve Eq. 1.85 for x_2 in terms of x_3 provided $a'_{22} \neq 0$; that is,

$$x_2 = \frac{b'_2 - a'_{23}x_3}{a'_{22}} \tag{1.88}$$

then substitute this x_2 into the last equation (Eq. 1.86) to obtain

$$a''_{33}x_3 = b''_3 \tag{1.89}$$

where

$$a''_{33} = a'_{33} - \frac{a'_{32}}{a'_{22}}a'_{23}; \quad b''_3 = b'_3 - \frac{a'_{32}}{a'_{22}}b'_2 \tag{1.90}$$

We see that the patterns of Eqs. 1.87 and 1.90 are exactly the same and this pattern is independent of the number of equations. This serial feature can be exploited in computer programming.

Thus, the elimination process finally yields one equation in terms of the variable x_3, from which it can be solved as

$$x_3 = \frac{b''_3}{a''_{33}} \tag{1.91}$$

By knowing x_3, x_2 can be obtained from Eq. 1.88, and finally x_1 from Eq. 1.84. This procedure is called back substitution.

1.10.2 Augmented Matrix

The elimination procedure described in the last section involves the manipulation of equations. No matter how we manipulate the equations, the final solution vector $\mathbf{x}$ is still the same. One way to simplify the elimination process is to set up an augmented matrix as

$$[\mathbf{A}|b] = \left[\begin{array}{ccc|c} a_{11} & a_{12} & a_{13} & b_1 \\ a_{21} & a_{22} & a_{23} & b_2 \\ a_{31} & a_{32} & a_{33} & b_3 \end{array}\right] \tag{1.92}$$

and then perform the row operations described in Section 1.9 to effect the elimination process.

EXAMPLE 1.1

Let us demonstrate this concept of an augmented matrix to the following example:

$$\begin{aligned} x_1 + 2x_2 + 3x_3 &= 14 \\ x_1 + x_2 - x_3 &= 0 \\ 2x_1 + x_2 - x_3 &= 1 \end{aligned} \tag{1.93}$$

For this set of three linear equations, we form an augmented matrix by putting the coefficient matrix first and then the RHS vector, shown as follows:

$$\left[\begin{array}{ccc|c} 1 & 2 & 3 & 14 \\ 1 & 1 & -1 & 0 \\ 2 & 1 & -1 & 1 \end{array}\right] \tag{1.94}$$

Now, we start carrying out row operations on the augmented matrix. First, we take the second row and subtract it from the first row to form a new second row, the result of which is shown as follows:

$$\left[\begin{array}{ccc|c} 1 & 2 & 3 & 14 \\ 0 & 1 & 4 & 14 \\ 2 & 1 & -1 & 1 \end{array}\right] \tag{1.95}$$

The purpose of the last step is to eliminate x_1 from the second equation; that is, the new coefficient for x_1 in the new second equation is 0. This is the basic step of elimination. Now, we do exactly the same to the third row. We multiply the first row by 2 and subtract the third row to form a new third row and get the result

$$\left[\begin{array}{ccc|c} 1 & 2 & 3 & 14 \\ 0 & 1 & 4 & 14 \\ 0 & 3 & 7 & 27 \end{array}\right] \tag{1.96}$$

Thus, we have eliminated the variable x_1 from the second and the third equations. Now, we move to the next step of the elimination procedure, that is, to remove the variable x_2 from the third equation. This is done by multiplying the second row by 3 and subtracting the third row to form a new third row; that is,

$$\left[\begin{array}{ccc|c} 1 & 2 & 3 & 14 \\ 0 & 1 & 4 & 14 \\ 0 & 0 & 5 & 15 \end{array}\right] \tag{1.97}$$

The last row will give a solution of $x_3 = 3$. Put this into the second equation to give $x_2 = 2$, and hence finally into the first equation to give $x_1 = 1$. This is the back substitution procedure. All the steps carried out are part of the Gauss elimination scheme. More details on this method will be presented in Section 1.10.5.

Let us now come back to our present example and continue with the row operations, but this time we eliminate the variables above the major diagonal line. To do this, we multiply the third row by $(-\frac{4}{5})$ and add the result to the second row to form a new second row, shown as follows:

$$\left[\begin{array}{ccc|c} 1 & 2 & 3 & 14 \\ 0 & 1 & 0 & 2 \\ 0 & 0 & 5 & 15 \end{array}\right] \tag{1.98}$$

The last step is to remove the variable x_3 from the second equation. Finally, multiply the second row by (-2) and the third row by $(-\frac{3}{5})$ and add the results to the first row to obtain a new first row as

$$\left[\begin{array}{ccc|c} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 2 \\ 0 & 0 & 5 & 15 \end{array}\right] \tag{1.99}$$

from which one can see immediately $x_1 = 1$, $x_2 = 2$ and $x_3 = 3$. The last few extra steps are part of the Gauss–Jordan elimination scheme, the main purpose of which is to obtain the inverse as we shall see in Section 1.10.6.

This procedure of augmented matrix can handle more than one vector **b** at the same time; for example, if we are to solve the following equations with the same coefficient matrix **A**: $\mathbf{A}\mathbf{x}_1 = \mathbf{b}_1$, $\mathbf{A}\mathbf{x}_2 = \mathbf{b}_2$, we can set the augmented matrix as

$$[\mathbf{A} \mid \mathbf{b}_1 \quad \mathbf{b}_2] \tag{1.100}$$

and carry out the row operations as we did in the last example to obtain simultaneously the solution vectors $\mathbf{x}_1$ and $\mathbf{x}_2$.

1.10.3 Pivoting

The elimination procedure we described in Section 1.10.1 requires that a_{11} is nonzero. Thus, if the diagonal coefficient a_{11} is zero, then we shall need to rearrange the equations, that is, we interchange the rows such that the new diagonal term a_{11} is nonzero. We also carry out this pivoting process in such a way that the element of largest magnitude is on the major diagonal line. If rows are interchanged only, the process is called partial pivoting, while if both rows and columns are interchanged it is called full pivoting. Full pivoting is not normally carried out because it changes the order of the components of the vector **x**. Therefore, only partial pivoting is dealt with here.

EXAMPLE 1.2

Partial pivoting not only eliminates the problem of zero on the diagonal line, it also reduces the round-off error since the pivot element (i.e., the diagonal element) is the divisor in the elimination process. To demonstrate the pivoting procedure, we use an example of three linear equations.

$$\begin{aligned} 0x_1 + x_2 + x_3 &= 5 \\ 4x_1 + x_2 - x_3 &= 3 \\ x_1 - x_2 + x_3 &= 2 \end{aligned} \tag{1.101}$$

Putting this set of equations into the augmented matrix form, we have

$$\left[\begin{array}{ccc|c} 0 & 1 & 1 & 5 \\ 4 & 1 & -1 & 3 \\ 1 & -1 & 1 & 2 \end{array}\right] \tag{1.102}$$

We note that the coefficient a_{11} is zero; therefore, there is a need to carry out the pivoting procedure. The largest element of the first column is 4. Therefore, upon interchanging the first and the second rows, we will get

$$\left[\begin{array}{ccc|c} 4 & 1 & -1 & 3 \\ 0 & 1 & 1 & 5 \\ 1 & -1 & 1 & 2 \end{array}\right] \tag{1.103}$$

Next, multiplying the third row by 4 and subtracting the first row to get the new third row will yield

$$\left[\begin{array}{ccc|c} 4 & 1 & -1 & 3 \\ 0 & 1 & 1 & 5 \\ 0 & -5 & 5 & 5 \end{array}\right] \tag{1.104}$$

Although the pivot element in the second row is 1 ($\neq 0$), it is not the largest element in that column (second column). Hence, we carry out pivoting again, and this process is done with rows underneath the pivot element, not with rows above it. This is because the rows above the pivot element have already gone through the elimination process. Using them will destroy the elimination completed so far.

Interchange the second and the third row so that the pivot element will have the largest magnitude, we then have

$$\left[\begin{array}{ccc|c} 4 & 1 & -1 & 3 \\ 0 & -5 & 5 & 5 \\ 0 & 1 & 1 & 5 \end{array}\right] \tag{1.105}$$

Next, multiply the third row by 5 and add with the second row to form a new third row, we get

$$\left[\begin{array}{ccc|c} 4 & 1 & -1 & 3 \\ 0 & -5 & 5 & 5 \\ 0 & 0 & 10 & 30 \end{array}\right] \tag{1.106}$$

Finally, using the back substitution, we find that $x_3 = 3$, $x_2 = 2$, and $x_1 = 1$.

1.10.4 Scaling

When the magnitude of elements in one or more equations are greater than the elements of the other equations, it is essential to carry out scaling. This is done by dividing the elements of each row, including the **b** vector, by the largest element of that row (excluding the b element). After scaling, pivoting is then carried out to yield the largest pivot element.

1.10.5 Gauss Elimination

The elimination procedure described in the last sections forms a process, commonly called Gauss elimination. It is the backbone of the direct methods, and is the most useful in solving linear equations. Scaling and pivoting are essential in the Gauss elimination process.

The Gauss elimination algorithm is summarized as follows:

Step 1: Augment the matrix $\mathbf{A}(N \times N)$ and the vector $\mathbf{b}$ $(N \times 1)$ to form an augmented matrix $\mathbf{A}$ of size $N \times (N+1)$.

Step 2: Scale the rows of the augmented matrix.

Step 3: Search for the largest element in magnitude in the first column and pivot that coefficient into the a_{11} position.

Step 4: Apply the elimination procedure to rows 2 to N to create zeros in the first column below the pivot element. The modified elements in row 2 to row N and column 2 to column $N+1$ of the augmented matrix must be computed and inserted in place of the original elements using the following formula:

$$a'_{ij} = a_{ij} - \frac{a_{i1}}{a_{11}} a_{1j}; \quad \text{for} \quad i = 2, 3, \ldots, N \quad \text{and} \quad j = 2, 3, \ldots, N+1 \tag{1.107}$$

Step 5: Repeat steps 3 and 4 for rows 3 to N. After this is completely done, the resulting augmented matrix will be an upper triangular matrix.

Step 6: Solve for $\mathbf{x}$ using back substitution with the following equations:

$$x_N = \frac{a'_{N,N+1}}{a'_{N,N}} \tag{1.108}$$

$$x_i = \frac{a'_{i,N+1} - \sum_{j=i+1}^{N} a'_{ij} x_j}{a'_{ii}} \quad \text{for} \quad i = N-1, N-2, \ldots, 1 \tag{1.109}$$

where a'_{ij} is an element of the augmented matrix obtained at the end of step 5.

1.10.6 Gauss–Jordan Elimination: Solving Linear Equations

Gauss–Jordan elimination is a variation of the Gauss elimination scheme. Instead of obtaining the triangular matrix at the end of the elimination, the Gauss–Jordan has one extra step to reduce the matrix **A** to an identity matrix. In this way, the augmented vector $\mathbf{b}'$ is simply the solution vector **x**.

The primary use of the Gauss–Jordan method is to obtain an inverse of a matrix. This is done by augmenting the matrix **A** with an identity matrix **I**. After the elimination process in converting the matrix **A** to an identity matrix, the right-hand side identity matrix will become the inverse $\mathbf{A}^{-1}$. To show this, we use the following example:

$$\left[\begin{array}{ccc|ccc} 1 & 1 & 1 & 1 & 0 & 0 \\ 2 & -1 & 1 & 0 & 1 & 0 \\ 1 & -2 & 2 & 0 & 0 & 1 \end{array}\right] \tag{1.110}$$

Interchange the first and the second row to make the pivot element having the largest magnitude; hence, we have

$$\left[\begin{array}{ccc|ccc} 2 & -1 & 1 & 0 & 1 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & -2 & 2 & 0 & 0 & 1 \end{array}\right] \tag{1.111}$$

Now, scale the pivot element to unity (this step is not in the Gauss elimination scheme) to give

$$\left[\begin{array}{ccc|ccc} 1 & -\frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & -2 & 2 & 0 & 0 & 1 \end{array}\right] \tag{1.112}$$

By following the same procedure of Gauss elimination with the extra step of normalizing the pivot element before each elimination, we finally obtain

$$\left[\begin{array}{ccc|ccc} 1 & -\frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} & 0 \\ 0 & 1 & \frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & 0 & 1 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \end{array}\right] \tag{1.113}$$

Now, we perform the elimination for rows *above* the pivot elements, and after this step the original **A** matrix becomes an identity matrix, and the original identity matrix **I** in the RHS of the augmented matrix becomes the matrix inverse $\mathbf{A}^{-1}$; that is,

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & 0 & \frac{2}{3} & -\frac{1}{3} \\ 0 & 1 & 0 & \frac{1}{2} & -\frac{1}{6} & -\frac{1}{6} \\ 0 & 0 & 1 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \end{array}\right] \tag{1.114}$$

Obtaining the matrix inverse using the Gauss–Jordan method provides a compact way of solving linear equations. For a given problem,

$$\mathbf{Ax} = \mathbf{b} \tag{1.115}$$

we multiply the equation by $\mathbf{A}^{-1}$, and obtain

$$\mathbf{A}^{-1}(\mathbf{Ax}) = \mathbf{A}^{-1}\mathbf{b} \tag{1.116}$$

Noting that the multiplication is associative; hence, we have

$$(\mathbf{A}^{-1}\mathbf{A})\mathbf{x} = \mathbf{A}^{-1}\mathbf{b}, \quad \text{i.e.,} \quad \mathbf{x} = \mathbf{A}^{-1}\mathbf{b} \tag{1.117}$$

Thus, this inverse method provides a compact way of presenting the solution of the set of linear equations.

1.10.7 LU Decomposition

In the LU decomposition method, the idea is to decompose a given matrix A to a product **LU**. If we specify the diagonal elements of either the upper or the lower triangular matrix, the decomposition will be unique. If the elements of the major diagonal of the **L** matrix are unity, the decomposition method is called the Doolittle method. It is called the Crout method if the elements of the major diagonal of the **U** matrix are unity.

In the Doolittle method, the upper triangular matrix **U** is determined by the Gauss elimination process, while the matrix **L** is the lower triangular matrix containing the multipliers employed in the Gauss process as the elements below the unity diagonal line. More details on the Doolittle and Crout methods can be found in Hoffman (1992).

The use of the LU decomposition method is to find solution to the linear equation $\mathbf{Ax} = \mathbf{b}$. Let the coefficient matrix **A** be decomposed to **LU**, that is, $\mathbf{A} = \mathbf{LU}$. Hence, the linear equation will become

$$\mathbf{LUx} = \mathbf{b} \tag{1.118}$$

Multiplying the above equation by $\mathbf{L}^{-1}$, we have

$$\mathbf{L}^{-1}(\mathbf{LU})\mathbf{x} = \mathbf{L}^{-1}\mathbf{b} \tag{1.119}$$

Since the multiplication is associative and $\mathbf{L}^{-1}\mathbf{L} = \mathbf{I}$, the previous equation will become

$$\mathbf{U}\mathbf{x} = \mathbf{b}' \tag{1.120}$$

where the vector $\mathbf{b}'$ is obtained from the equation

$$\mathbf{L}\mathbf{b}' = \mathbf{b} \tag{1.121}$$

Equations 1.120 and 1.121 will form basic set of equations for solving for $\mathbf{x}$. This is done as follows. For a given $\mathbf{b}$ vector, the vector $\mathbf{b}'$ is obtained from Eq. 1.121 by forward substitution since $\mathbf{L}$ is the lower triangular matrix. Once $\mathbf{b}'$ is found, the desired vector $\mathbf{x}$ is found from Eq. 1.120 by backward substitution because $\mathbf{U}$ is the upper triangular matrix.

1.11 ITERATIVE METHODS

When dealing with large sets of equations, especially if the coefficient matrix is sparse, the iterative methods provide an attractive option in getting the solution. In the iterative methods, an initial solution vector $\mathbf{x}^{(0)}$ is assumed, and the process is iterated to reduce the error between the iterated solution $\mathbf{x}^{(k)}$ and the exact solution $\mathbf{x}$, where k is the iteration number. Since the exact solution is not known, the iteration process is stopped by using the difference $\Delta x_i = x_i^{(k+1)} - x_i^{(k)}$ as the measure. The iteration is stopped when one of the following criteria has been achieved.

$$\left|\frac{(\Delta x_i)_{\max}}{x_i}\right| < \varepsilon; \quad \sum_{i=1}^{N}\left|\frac{\Delta x_i}{x_i}\right| < \varepsilon; \quad \left[\sum_{i=1}^{N}\left(\frac{\Delta x_i}{x_i}\right)^2\right]^{1/2} < \varepsilon \tag{1.122}$$

The disadvantage of the iterative methods is that they may not provide a convergent solution. Diagonal dominance (Eqs. 1.59 and 1.60) is the sufficient condition for convergence. The stronger the diagonal dominance the fewer number of iterations required for the convergence.

There are three commonly used iterative methods that we will briefly present here. They are Jacobi, Gauss–Seidel, and the successive overrelaxation methods.

1.11.1 Jacobi Method

The set of linear equations written in the component form is

$$b_i - \sum_{j=1}^{N} a_{ij}x_j = 0 \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.123}$$

Divide the equation by a_{ii} and add x_i to the LHS and RHS to yield the equation

$$x_i = x_i + \frac{1}{a_{ii}}\left(b_i - \sum_{j=1}^{N} a_{ij}x_j = 0\right) \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.124}$$

The iteration process starts with an initial guessing vector $\mathbf{x}^{(0)}$, and the iteration equation used to generate the next iterated vector is

$$x_i^{(k+1)} = x_i^{(k)} + \frac{1}{a_{ii}}\left(b_i - \sum_{j=1}^{N} a_{ij}x_j^{(k)} = 0\right) \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.125}$$

The iteration process will proceed until one of the criteria in Eq. 1.122 has been achieved.

The second term in the RHS of Eq. 1.125 is called the residual, and the iteration process will converge when the residual is approaching zero for all values of i.

1.11.2 Gauss–Seidel Iteration Method

In the Jacobi method, the iterated vector of the $(k+1)$th iteration is obtained based entirely on the vector of the previous iteration, that is, $\mathbf{x}^{(\mathrm{k})}$. The Gauss–Seidel iteration method is similar to the Jacobi method, except that the component $x_j^{(k+1)}$ for $j = 1, 2, \ldots, i-1$ are used immediately in the calculation of the component $x_i^{(k+1)}$. The iteration equation for the Gauss–Seidel method is

$$x_i^{(k+1)} = x_i^{(k)} + \frac{1}{a_{ii}} \times \left(b_i - \sum_{j=1}^{i-1} a_{ij}x_j^{(k+1)} - \sum_{j=i}^{N} a_{ij}x_j^{(k)} = 0\right) \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.126}$$

Like the Jacobi method, the Gauss–Seidel method requires diagonal dominance for the convergence of iterated solutions.

1.11.3 Successive Overrelaxation Method

In many problems, the iterated solutions approach the exact solutions in a monotonic fashion. Therefore, it is useful in this case to speed up the convergence process by overrelaxing the iterated solutions. The equation for the overrelaxation scheme is modified from the Gauss–Seidel equation

$$x_i^{(k+1)} = x_i^{(k)} + \frac{w}{a_{ii}} \times \left(b_i - \sum_{j=1}^{i-1} a_{ij} x_j^{(k+1)} - \sum_{j=i}^{N} a_{ij} x_j^{(k)} = 0 \right) \quad \text{for} \quad i = 1, 2, \ldots, N \tag{1.127}$$

where w is the overrelaxation factor. When $w = 1$, we recover the Gauss–Seidel method. When $1 < w < 2$, we have an overrelaxation situation. When $w < 1$, the system is underrelaxed. The latter is applicable when the iteration provides oscillatory behavior. When $w > 2$, the method diverges.

There is no fast rule on how to choose the optimum w for a given problem. It must be found from numerical experiments.

1.12 SUMMARY OF THE MODEL BUILDING PROCESS

These introductory examples are meant to illustrate the essential qualitative nature of the early part of the model building stage, which is followed by more precise quantitative detail as the final image of the desired model is made clearer. It is a property of the human condition that minds change as new information becomes available. Experience is an important factor in model formulation, and there have been recent attempts to simulate the thinking of experienced engineers through a format called *Expert Systems*. The following step-by-step procedure may be useful for beginners:

1. Draw a sketch of the system to be modeled and label/define the various geometric, physical, and chemical quantities.
2. Carefully select the important dependent (response) variables.
3. Select the possible independent variables (e.g., z,t), changes in which must necessarily affect the dependent variables.
4. List the parameters (physical constants, physical size, and shape) that are expected to be important; also note the possibility of nonconstant parameters (e.g., viscosity changing with temperature, $\mu(T)$).
5. Draw a sketch of the expected behavior of the dependent variable(s), such as the “expected” temperature profile we used for illustrative purposes in Fig. 1.3.
6. Establish a “control volume” for a differential or finite element (e.g., CSTR) of the system to be modeled; sketch the element and indicate all inflow–outflow paths.
7. Write the “conservation law” for the volume element: Write flux and reaction rate terms using general symbols, which are taken as positive quantities, so that signs are introduced only as terms are inserted according to the rules of the conservation law, Eq. 1.1.
8. After rearrangement into the proper differential format, invoke the fundamental lemma of calculus to produce a differential equation.
9. Introduce specific forms of flux (e.g., $J_r = -D\partial C/\partial r$) and rate ($R_A = kC_A$); note the opposite of generation is depletion, so when a species is depleted, its loss rate must be entered with the appropriate sign in the conservation law (i.e., replace “+ generation” with “− depletion” in Eq. 1.1).
10. Write down all possibilities for boundary values of the dependent variables; the choice among these will be made in conjunction with the solution method selected for the defining (differential) equation.
11. Search out solution methods, and consider possible approximations for (i) the defining equation, (ii) the boundary conditions, and (iii) an acceptable final solution.
12. Introduce a vector–matrix format for coupled linear equations.

It is clear that the modeling and solution effort should go hand in hand, tempered of course by available experimental and operational evidence.

1.13 MODEL HIERARCHY AND ITS IMPORTANCE IN ANALYSIS

As pointed out in Section 1.1 regarding the real purposes of the modeling effort, the scope and depth of these decisions will determine the complexity of the mathematical description of a process. If we take the scope and depth as the barometer for generating models, we will obtain a hierarchy of models where the lowest level may be regarded as a black box and the highest is where all possible transport processes known to man in addition to all other concepts (such as thermodynamics) are taken into account. Models, therefore, do not appear in isolation, but rather they belong to a family where the hierarchy is dictated by the number of rules (transport principles, thermodynamics). It is this family that provides engineers with capabilities to predict and understand the phenomena

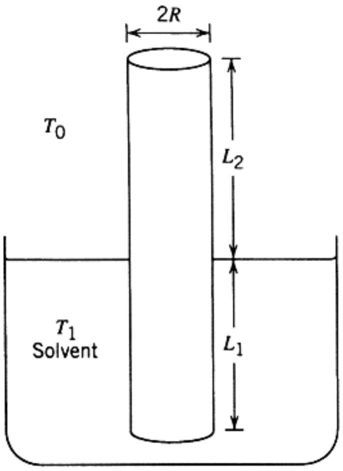


FIGURE 1.4 Schematic diagram of heat removal from a solvent bath.

around us. The example of cooling of a fluid flowing in a tube (Models I and II) in Section 1.2 illustrated two members of this family. As the level of sophistication increased, the mathematical complexity increased. If one is interested in exactly how heat is conducted through the metal casing and is disposed of to the atmosphere, then the complexity of the problem must be increased by writing down a heat balance relation for the metal casing (taking it to be constant at a value T_w is, of course, a model, albeit the simplest one). Furthermore, if one is interested in how the heat is transported near the entrance section, one must write down heat balance equations before the start of the tube, in addition to Eq. 1.31 for the active, cooling part of the tube. In addition, the nature of the boundary conditions must be carefully scrutinized before and after the entrance zone in order to properly describe the boundary conditions.

To further demonstrate the concept of model hierarchy and its importance in analysis, let us consider a problem of heat removal from a bath of hot solvent by immersing steel rods into the bath and allowing the heat to dissipate from the hot solvent bath through the rod and thence to the atmosphere (Fig. 1.4).

For this elementary problem, it is wise to start with the simplest model first to get some feel about the system response.

Level 1

In this level, let us assume that

(a) the rod temperature is uniform, that is, from the bath to the atmosphere;
(b) ignore heat transfer at the two flat ends of the rod;
(c) overall heat transfer coefficients are known and constant;
(d) no solvent evaporates from the solvent air interface.

The many assumptions listed above are necessary to simplify the analysis (i.e., to make the model tractable).

Let T_0 and T_1 be the atmosphere and solvent temperatures, respectively. The steady-state heat balance (i.e., no accumulation of heat by the rod) shows a balance between heat collected in the bath and that dissipated by the upper part of the rod to atmosphere

$$h_L(2\pi RL_1)(T_1 - T) = h_G(2\pi RL_2)(T - T_0) \qquad (1.128)$$

where T is the temperature of the rod, and L_1 and L_2 are lengths of rod exposed to solvent and to atmosphere, respectively. Obviously, the volume elements are finite (not differential), being composed of the volume above the liquid of length L_2 and the volume below of length L_1.

Solving for T from Eq. 1.126 yields

$$T = \frac{(T_0 + \alpha T_1)}{(1+\alpha)} \qquad (1.129)$$

where

$$\alpha = \frac{h_L L_1}{h_G L_2} \qquad (1.130)$$

Equation 1.129 gives us a very quick estimate of the rod temperature and how it varies with exposure length. For example, if α is much greater than unity (i.e., long $\mathbf{L}_1$ section and high liquid heat transfer coefficient compared to gas coefficient), the rod temperature is then very near T_1. Taking the rod temperature to be represented by Eq. 1.129, the rate of heat transfer is readily calculated from Eq. 1.128 by replacing T:

$$\begin{aligned} Q &= \frac{h_L 2\pi R L_1}{(1+\alpha)}(T_1 - T_0) \\ &= \frac{h_L L_1}{(1 + (h_L L_1/h_G L_2))} 2\pi R (T_1 - T_0) \end{aligned} \qquad (1.131a)$$

$$Q = \frac{1}{((1/h_L L_1) + (1/h_G L_2))} 2\pi R (T_1 - T_0) \qquad (1.131b)$$

When $\alpha = h_L L_1/h_G L_2$ is very large, the rate of heat transfer becomes simply

$$Q \cong 2\pi R h_G L_2 (T_1 - T_0) \qquad (1.131c)$$

Thus, the heat transfer is controlled by the segment of the rod exposed to the atmosphere. It is interesting to note that when the heat transfer coefficient contacting the solvent is very high (i.e., $\alpha \gg 1$), it does not really matter how much of the rod is immersed in the solvent.

Thus for a given temperature difference and a constant rod diameter, the rate of heat transfer can be enhanced by either increasing the exposure length L_2 or by increasing the heat transfer rate by blowing air over the exposed rod. However, these conclusions are tied to the assumption of constant rod temperature, which becomes tenuous as atmospheric exposure is increased.

To account for effects of temperature gradients in the rod, we must move to the next level in the model hierarchy, which is to say that a differential volume must be considered.

Level 2

Let us relax part of the assumption (a) of the first model by assuming only that the rod temperament below the solvent liquid surface is uniform at a value T_1. This is a reasonable proposition, since the liquid has a much higher thermal conductivity than air. The remaining three assumptions of the level 1 model are retained.

Next, choose an upward pointing coordinate x with the origin at the solvent–air surface. Figure 1.5 shows the coordinate system and the elementary control volume.

Applying a heat balance around a thin shell segment with thickness Δx gives

$$\pi R^2 q(x) - \pi R^2 q(x+\Delta x) - 2\pi R \Delta x h_G (T - T_0) = 0 \tag{1.132}$$

where the first and the second terms represent heat conducted into and out of the element and the last term represents heat loss to atmosphere. We have concluded, by writing this, that temperature gradients are likely to exist in the part of the rod exposed to air, but are unlikely to exist in the submerged part.

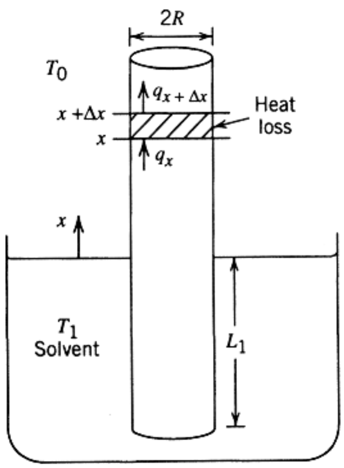


FIGURE 1.5 Shell element and the system coordinate.

Dividing Eq. 1.132 by $\pi R^2 \Delta x$ and taking the limit as $\Delta x \to 0$ yields the following first-order differential equation for the heat flux, q:

$$\frac{dq}{dx} + \frac{2}{R} h_G (T - T_0) = 0 \tag{1.133}$$

Assuming the rod is homogeneous, that is, the thermal conductivity is uniform, the heat flux along the axis is related to the temperature according to Fourier's law of heat conduction (Eq. 1.29). Substitution of Eq. 1.29 into Eq. 1.133 yields

$$k\frac{d^2T}{dx^2} = \frac{2h_G}{R}(T - T_0)a \tag{1.134}$$

Equation 1.134 is a second-order ordinary differential equation, and to solve this, two conditions must be imposed. One condition was stipulated earlier:

$$x = 0, \quad T = T_1 \tag{1.135a}$$

The second condition (heat flux) can also be specified at $x = 0$ or at the other end of the rod, that is, $x = L_2$. Heat flux is the sought-after quantity, so it cannot be specified *a priori*. One must then provide a condition at $x = L_2$. At the end of the rod, one can assume Newton's law of cooling prevails, but since the rod length is usually longer than the diameter, most of the heat loss occurs at the rod's lateral surface, and the flux from the top surface is small, so write approximately:

$$x = L_2; \quad \frac{dT}{dx} \simeq 0 \tag{1.135b}$$

Equation 1.134 is subjected to the two boundary conditions (Eq. 1.135) to yield the solution

$$T = T_0 + (T_1 - T_0)\frac{\cosh[m(L_2 - x)]}{\cosh(mL_2)} \tag{1.136}$$

where

$$m = \sqrt{\frac{2h_G}{Rk}} \tag{1.137}$$

We will discuss the method of solution of such second-order equations in Chapter 2.

Once we know the temperature distribution of the rod above the solvent–air interface, then the rate of heat loss can be calculated either of two ways. In the first, we know

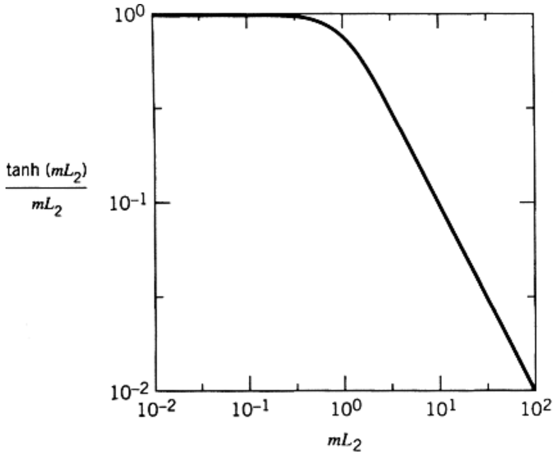


FIGURE 1.6 A plot of the effectiveness factor versus mL_2.

that the heat flow through area πR^2 at $x=0$ must be equal to the heat released into the atmosphere, that is,

$$Q = -\pi R^2 k \left.\frac{\partial T}{\partial x}\right|_{x=0} \tag{1.138}$$

Applying Eq. 1.136 to Eq. 1.138 gives

$$Q = 2\pi R h_G L_2 \eta (T_1 - T_0) \tag{1.139a}$$

where

$$\eta = \frac{\tanh(mL_2)}{mL_2}$$

This dimensionless group (called *effectiveness factor*) represents the ratio of actual heat loss to the (maximum) loss rate when gradients are absent.

Figure 1.6 shows the log–log plot of η versus the dimensionless group mL_2. We note that the effectiveness factor approaches unity when mL_2 is much less than unity and it behaves like $1/mL_2$ as mL_2 is very large.

In the limit for small mL_2, we can write

$$\eta = \frac{\tanh(mL_2)}{mL_2} \approx 1 \tag{1.139b}$$

which is the most effective heat transfer condition. This is physically achieved when

(a) Rod thermal conductivity is large.
(b) Segment exposed to atmosphere (L_2) is short.

For such a case, we can write the elementary result

$$Q = 2\pi R h_G L_2 (T_1 - T_0) \tag{1.140}$$

which is identical to the first model (Eq. 1.131c). Thus, we have learned that the first model is valid only when $mL_2 \ll 1$. Another way of calculating the heat transfer rate is carrying out the integration of local heat transfer rate along the rod

$$Q = \int_0^{L_2} dq = \int_0^{L_2} h_G (T - T_0)(2\pi R dx) \tag{1.141}$$

where T is given in Eq. 1.136 and the differential transfer area is $2\pi R dx$. Substituting T of Eq. 1.136 into Eq. 1.141 yields the same solution for Q as given in Eq 1.139a.

Levels 1 and 2 solutions have one assumption in common: The rod temperature below the solvent surface was taken to be uniform. The validity of this modeling assumption will not be known until we move up one more level in the model hierarchy.

Level 3

In this level of modeling, we relax the assumption (a) of the first level by allowing for temperature gradients in the rod for segments above and below the solvent–air interface.

Let the temperature below the solvent–air interface be T^{I} and that above the interface be T^{II}. Carrying out the one-dimensional heat balances for the two segments of the rod, we obtain

$$\frac{d^2 T^{\mathrm{I}}}{dx^2} = \frac{2h_L}{Rk}(T^{\mathrm{I}} - T_1) \tag{1.142}$$

and

$$\frac{d^2 T^{\mathrm{II}}}{dx^2} = \frac{2h_G}{Rk}(T^{\mathrm{II}} - T_0) \tag{1.143}$$

We shall still maintain the condition of zero flux at the flat ends of the rod. This means of course that

$$x = -L_1; \quad \frac{dT^{\mathrm{I}}}{dx} = 0 \tag{1.144}$$

$$x = L_2; \quad \frac{dT^{\mathrm{II}}}{dx} = 0 \tag{1.145}$$

Equations 1.144 and 1.145 provide two of the four necessary boundary conditions. The other two arise from the continuity of temperature and flux at the $x=0$ position, that is,

$$x = 0; \quad T^{\mathrm{I}} = T^{\mathrm{II}} \tag{1.146a}$$

$$x = 0; \quad \frac{dT^{\mathrm{I}}}{dx} = \frac{dT^{\mathrm{II}}}{dx} \tag{1.146b}$$

Solutions of Eqs. 1.142 and 1.143 subject to conditions 1.144 and 1.145 are easily obtained by methods illustrated in the next chapter (Example 2.25)

$$T^{\mathrm{I}} = T_1 + A\cosh[n(x+L_1)] \tag{1.147}$$

and

$$T^{\mathrm{II}} = T_0 + B\cosh[m(L_2 - x)] \tag{1.148}$$

where m is defined in Eq. 1.137 and a new ratio is

$$n = \sqrt{\frac{2h_L}{Rk}} \tag{1.149}$$

The constants of integration, A and B, can be found by substituting Eqs. 1.147 and 1.148 into the continuity conditions (1.146a, b) to finally get

$$B = \frac{(T_1 - T_0)}{[\cosh(mL_2) + (m/n)(\sinh(mL_2)/\sinh(nL_1))\cosh(nL_1)]} \tag{1.150}$$

$$A = -\frac{(T_1 - T_0)}{[\cosh(nL_1) + (n/m)(\sinh(nL_1)/\sinh(mL_2))\cosh(mL_2)]} \tag{1.151}$$

The rate of heat transfer can be obtained by using either of the two ways mentioned earlier, that is, using flux at $x=0$, or by integrating around the lateral surface. In either case, we obtain

$$Q = -\pi R^2 k \frac{dT^{\mathrm{I}}(0)}{dx} \tag{1.152}$$

$$Q = 2\pi R h_G L_2 \eta \frac{(T_1 - T_0)}{[1 - (m\tanh(mL_2)/n\tanh(nL_1))]} \tag{1.153}$$

where the effectiveness factor η is defined in Eq. 1.139.

You may note the difference between the solution obtained by the level 2 model and that obtained in the third level. Because of the allowance for temperature gradients (which represents the rod's resistance to heat flow) in the segment underneath the solvent surface, the rate of heat transfer calculated at this new level is less than that calculated by the level 2 model where the rod temperature was taken to be uniform at T_1 below the liquid surface.

This implies from Eq. 1.153 that the heat resistance in the submerged region is negligible compared to that above the surface only when

$$\frac{m\tanh(mL_2)}{n\tanh(nL_1)} \ll 1 \tag{1.154}$$

When the criterion (1.154) is satisfied, the rate of heat transfer given by Model II is valid. This is controlled mainly by the ratio $m/n = (h_G/h_L)^{1/2}$, which is always less than unity.

What we have seen in this exercise is simply that higher levels of modeling yield more information about the system and hence provide needed criteria to validate the model one level lower. In our example, the level 3 model provides the criterion (1.154) to indicate when the resistance to heat flow underneath the solvent bath can be ignored compared to that above the surface, and the level 2 model provides the criterion (1.139b) to indicate when there is negligible conduction resistance in the steel rod.

The next level of modeling is by now obvious: At what point and under what conditions do radial gradients become significant? This moves the modeling exercise into the domain of partial differential equations.

Level 4

Let us investigate the fourth level of model where we include radial heat conduction. This is important if the rod diameter is large relative to length. Let us assume in this model that there is no resistance to heat flow underneath the solvent interface, so as before, take temperature $T = T_1$ when $x \le 0$. This then leaves only the portion above the solvent surface to study.

Setting up the annular shell shown in Fig. 1.7 and carrying a heat balance in the radial and axial directions, we obtain the following heat conduction equation:

$$\begin{aligned}(2\pi r\Delta x q_r)|_r &- (2\pi r\Delta x q_r)|_{r+\Delta r} \\ &+ (2\pi r\Delta r q_x)|_x - (2\pi r\Delta r q_x)|_{x+\Delta x} = 0\end{aligned}$$

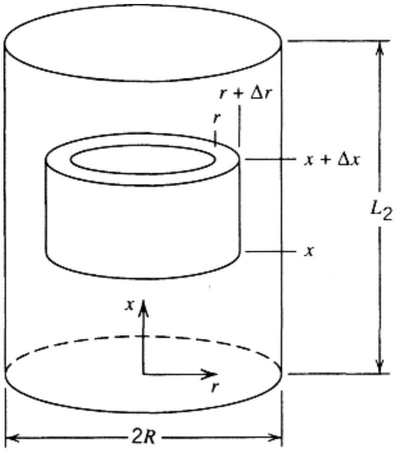


FIGURE 1.7 Schematic diagram of shell for heat balance.

Dividing this equation by $2\pi\Delta r\Delta x$ and taking limits, we obtain

$$-\frac{\partial}{\partial r}(rq_r) - r\frac{\partial q_x}{\partial x} = 0$$

Next, insert the two forms of Fourier's laws

$$q_r = -k\frac{\partial T}{\partial r}; \quad q_x = -k\frac{\partial T}{\partial x}$$

and get finally,

$$k\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial x^2}\right] = 0 \tag{1.155}$$

Here, we have assumed that the conductivity of the steel rod is isotropic and constant, that is, the thermal conductivity k is uniform in both x and r directions, and does not change with temperature.

Equation 1.155 is an elliptic partial differential equation. The physical boundary conditions to give a suitable solution are the following:

$$r = 0, \quad \frac{\partial T}{\partial r} = 0 \tag{1.156a}$$

$$r = R; \quad -k\frac{\partial T}{\partial r} = h_G(T - T_0) \tag{1.156b}$$

$$x = 0; \quad T = T_1 \tag{1.156c}$$

$$x = L_2; \quad \frac{\partial T}{\partial x} = 0 \tag{1.156d}$$

Equation 1.156a implies symmetry at the center of the rod, whereas at the curved outer surface of the rod the usual Newton cooling condition is applicable (Eq. 1.156b). Equation 1.156d states that there is no heat flow across the flat end of the rod. This is tantamount to saying that either the flat end is insulated or the flat end area is so small compared to the curved surface of the rod that heat loss there is negligible. Solutions for various boundary conditions can be found in Carslaw and Jaeger (1959).

When dealing with simple equations (as in the previous three models), the dimensional equations are solved without recourse to the process of nondimensionalization. Now, we must deal with partial differential equations, and both to simplify the notation during the analysis and to deduce the proper dimensionless parameters, it is necessary to reduce the equations to nondimensional form. To achieve this, we introduce the following nondimensional variables and parameters:

$$u = \frac{T - T_0}{T_1 - T_0}, \xi = \frac{r}{R}, \zeta = \frac{x}{L_2} \tag{1.157a}$$

$$\Delta = \left(\frac{R}{L_2}\right), \quad Bi = \frac{h_G R}{k} \quad \text{(Biot number)} \tag{1.157b}$$

where it is clear that only two dimensionless parameters arise: Δ and Bi. The dimensionless heat transfer coefficient $(h_G R/k)$, called the *Biot number*, represents the ratio of convective film transfer to conduction in the metal rod.

The nondimensional relations now become

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial u}{\partial \xi}\right) + \Delta^2\frac{\partial^2 u}{\partial \zeta^2} = 0 \tag{1.158}$$

$$\xi = 0; \quad \frac{\partial u}{\partial \xi} = 0 \tag{1.159a}$$

$$\xi = 1; \quad \frac{\partial u}{\partial \xi} = -Bi\, u \tag{1.159b}$$

$$\zeta = 0; \quad u = 1 \tag{1.159c}$$

$$\zeta = 1; \quad \frac{\partial u}{\partial \zeta} = 0 \tag{1.159d}$$

It is clear that these independent variables (j and z) are defined relative to the maximum possible lengths for the r and x variables, R and L_2, respectively. However, the way u (nondimensional temperature) is defined is certainly not unique. One could easily define u as follows

$$u = \frac{T}{T_0} \quad \text{or} \quad u = \frac{T}{T_1}$$

or (1.160)

$$u = \frac{T - T_0}{T_0} \quad \text{or} \quad u = \frac{T - T_0}{T_1}$$

and so on. There are good reasons for the selection made here, as we discuss in Chapters 10 and 11. The solution of Eq. 1.158 subject to boundary conditions (1.159) is given in Chapter 11 and its expression is given here only to help illustrate model hierarchy. The solution u is

$$u = \frac{T - T_0}{T_1 - T_0} = \sum_{n=1}^{\infty}\frac{\langle 1, K_n\rangle}{\langle K_n, K_n\rangle}K_n(\xi)\frac{\cosh[(\beta_n/\Delta)(1-\zeta)]}{\cosh[\beta_n/\Delta]} \tag{1.161}$$

where the functions are defined as

$$K_n(\xi) = J_0(\beta_n \xi) \tag{1.162a}$$

and the many characteristic values (eigenvalues) are obtained by trial and error from

$$\beta_n J_1(\beta_n) = Bi\, J_0(\beta_n) \tag{1.162b}$$

The other functional groups are defined as

$$\langle 1, K_n \rangle = \frac{J_1(\beta_n)}{\beta_n} \tag{1.162c}$$

$$\langle K_n, K_n \rangle = \frac{J_1^2(\beta_n)}{2}\left[1 + \left(\frac{\beta_n}{Bi}\right)^2\right] \tag{1.162d}$$

where $J_0(\beta)$ and $J_1(\beta)$ are tabulated relations called Bessel functions, which are discussed at length in Chapter 3. The rate of heat transfer can be calculated using the heat flux entering at position $x = 0$, but we must also account for radial variation of temperature so that the elemental area is $2\pi r dr$; thus, integrating over the whole base gives

$$Q = \int_0^R \left[-k\frac{\partial T}{\partial x}\right]_{x=0} 2\pi r dr \tag{1.163}$$

Putting this in nondimensional form, we have

$$Q = \frac{2\pi R^2 k}{L_2}(T_1 - T_0)\int_0^1 \left(-\frac{\partial u(0)}{\partial \xi}\right)\xi\, d\xi \tag{1.164}$$

By inserting dimensionless temperature from Eq. 1.161, we obtain the following somewhat complicated result for heat transfer rate:

$$Q = \frac{2\pi R^2 k(T_1 - T_0)}{L_2 \Delta}\sum_{n=1}^{\infty}\frac{\beta_n \langle 1, K_n\rangle^2}{\langle K_n, K_n\rangle}\tanh\left(\frac{\beta_n}{\Delta}\right) \tag{1.165}$$

This illustrates how complexity grows quickly as simplifications are relaxed.

For small $Bi \ll 1$, it is not difficult to show from the transcendental equation (1.162b) that the smallest eigenvalue is

$$\beta_1 \cong (2Bi)^{1/2} \tag{1.166}$$

By substituting this into Eq. 1.165, we will obtain Eq. 1.139a. Thus, the fourth model shows that the radial heat conduction inside the rod is unimportant when

$$Bi \ll 1 \tag{1.167}$$

In summary, we have illustrated how proper model hierarchy sets limits on the lower levels. In particular, one can derive criteria (like Eq. 1.167) to show when the simpler models are valid. Some solutions for the simpler models can be found in Walas (1991).

The obvious question arises: When is a model of a process good enough? This is not a trivial question, and it can be answered fully only when the detailed economics of design and practicality are taken into account. Here, we have simply illustrated the hierarchy of one simple process, and how to find the limits of validity of each more complicated model in the hierarchy. In the final analysis, the user must decide when tractability is more important than precision.

PROBLEMS

1.1$_1$. Length Required for Cooling Coil

A cooling coil made of copper tube is immersed in a regulated constant temperature bath held at a temperature of 20°C. The liquid flowing through the tube enters at 22°C, and the coil must be sufficiently long to ensure the exit liquid sustains a temperature of 20.5°C. The bath is so well stirred that heat transfer resistance at the tube–bath interface is minimal, and the copper wall resistance can also be ignored. Thus, the tube wall temperature can be taken equal to the bath temperature. Use Eq. 1.17 to estimate the required tube length (L) under the following conditions for the flowing liquid:

$C_p = 1$ kcal/kg ·°C
$R = 0.01$ m
$v_0 = 1$ m/s
$\rho = 10^3$ kg/m^3
$\mu = 0.001$ kg/m · s
$k = 1.43 \times 10^{-4}$ kcal/(s · m · K)

Since the Reynolds number is in the turbulent range, use the correlation of Sieder and Tate (Bird et al. 1960) to calculate h

$$Nu = 0.026\, Re^{0.8} Pr^{1/3}$$

where

$$Nu = \frac{hD}{k} \quad (D = 2R) \quad \text{(Nusselt number)}$$

$$Pr = \frac{C_p \mu}{k} \quad \text{(Prandtl number)}$$

$$Re = \frac{D v_0 \rho}{\mu} \quad \text{(Reynolds number)}$$

Answer: $(L/D) = 353.5$

1.2_2. Cooling of Fluids in Tube Flow: Locally Varying h
Apply the conditions of Model I (plug flow) and rederive the expression for temperature change when the heat transfer coefficient is not constant but varies according to the law

$$h = \gamma/\sqrt{z}$$

Answer: $\psi = \exp(-2\beta\sqrt{z}), \quad \beta = (2\pi R\gamma)/(v_0 A\rho C_p)$

1.3_2. Dissolution of Benzoic Acid
Initially, pure water is passed through a tube constructed of solid benzoic acid. Since benzoic acid is slightly soluble in water (denote solubility as C^* moles acid/cm^3 solution), the inner walls of the tube will dissolve very slowly. By weighing the dried tube before and after exposure, it is possible to calculate the rate of mass transfer.

(a) Take a quasi-steady-state material balance for plug velocity profiles and show that the ODE obtained is

$$-v_0\frac{dC}{dx} + k_C\left(\frac{4}{D}\right)(C^* - C) = 0$$

where D denotes the inner tube diameter (taken as approximately invariant), v_0 is liquid velocity, and k_C is the (constant) mass transfer coefficient.

(b) Define $\theta = (C - C^*)$ and show that the solution to part (a) is

$$\theta = K\exp\left(-\frac{4}{D}\frac{k_C}{v_0}x\right)$$

(c) If pure water enters the tube, evaluate K and obtain the final result

$$\frac{C(x)}{C^*} = 1 - \exp\left(-\frac{4}{D}\frac{k_C}{v_0}x\right)$$

(d) If the tube is allowed to dissolve for a fixed time Δt, show that the weight change can be calculated from

$$\Delta W = M_B C^* \Delta t v_0\left(\frac{\pi}{4}D^2\right)\left[1 - \exp\left(-\frac{4}{D}\frac{k_C}{v_0}L\right)\right]$$

where L is tube length and M_B is molecular weight acid.

(e) Rearrange the result in part (d) to solve directly for k_C, under condition when $4k_C L/Dv_0 < 1$, and show

$$k_C \approx \frac{\Delta W}{[M_B C^* \Delta t \pi D L]}$$

(f) Discuss the assumptions implied in the above analysis and deduce a method of estimating the maximum possible experimental error in calculating k_C; note experimental quantities subject to significant errors are ΔW, Δt, and D.

1.4_1. Lumped Thermal Model for Thermocouple
We wish to estimate the dynamics of a cold thermocouple probe suddenly placed in a hot flowing fluid stream for the purpose of temperature measurement. The probe consists of two dissimilar metal wires joined by soldering at the tip, and the wires are then encased in a metal sheath and the tip is finally coated with a bead of plastic to protect it from corrosion. Take the mass of the soldered tip plus plastic bead to be m, with specific heat C_p. Denote the transfer coefficient as h.

(a) If the effects of thermal conductivity can be ignored, show that the temperature response of the probe is described by

$$mC_p\frac{dT}{dt} = hA(T_f - T)$$

where A denotes the exposed area of probe tip, and $T(t)$ is its temperature.

(b) Lump the explicit parameters to form the system time constant, and for constant T_f, define a new variable $\theta = (T_f - T)$ and show that the compact form results

$$\tau\frac{d\theta}{dt} = -\theta$$

where the system time constant is defined as

$$\tau = \frac{mC_p}{hA} \quad \text{(s)}$$

(c) Integrate the expression in (b), using the initial condition $T(0) = T_0$ and show that

$$\frac{T - T_f}{T_0 - T_f} = \exp\left(-\frac{t}{\tau}\right)$$

(d) Rearrange the expression in (c) to obtain

$$\frac{T_0 - T}{T_0 - T_f} = 1 - \exp\left(-\frac{t}{\tau}\right)$$

and thus show the temperature excess is 63% of the final steady-state value after a time equivalent to one time constant has elapsed. This also represents a quick and easy way to deduce system time constants based on an elementary experiment.

1.5$_3$. Distributed Thermal Model for Thermocouple

If the plastic bead covering the tip of the thermocouple described in Problem 1.4 is quite large, and since plastic usually sustains a very low value of thermal conductivity, then the simple lumped model solution becomes quite inaccurate. To improve the model, we need to account for thermal conductivity in the (assumed) spherical shape of the plastic bead.

(a) Assuming the bead is a perfect sphere, contacted everywhere by external fluid of temperature T_f, perform a shell balance on an element of volume $4\pi r^2 \Delta r$ and show that

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right)$$

(b) Perform an elemental heat balance at the surface of the sphere and deduce

$$-k \frac{\partial T}{\partial r} = h(T - T_f) \quad \text{at} \quad r = R$$

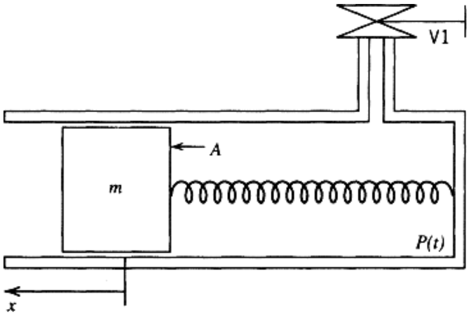
where R is the radius of the plastic sphere.

1.6$_2$. Modeling of Piston with Retaining Spring

The schematic figure shows a piston fitted snugly into a cylinder. The piston is caused to move by increasing or decreasing pressure P. As air is admitted by way of valve V1, the increased pressure drives the piston to the left, while the attached spring exerts a force to restrain the piston. At the same time, a highly viscous lubricant sealant at the juncture of piston and cylinder exerts a resisting force to damp the piston movement; the forces can be represented by

$$F_\mu = \alpha\mu \frac{dx}{dt}; \quad \mu = \text{lubricant viscosity}$$

$$F_x = Kx; \qquad K = \text{spring constant}$$



(a) Perform a force balance on the piston and show that

$$m \frac{d^2x}{dt^2} + \alpha\mu \frac{dx}{dt} + Kx = AP(t)$$

(b) Arrange this equation to obtain the standard form of the damped inertial equation:

$$\tau^2 \frac{d^2x}{dt^2} + 2\zeta\tau \frac{dx}{dt} + x = f(t)$$

and hence, deduce an expression for damping coefficient z and time constant τ. Such equations are used to model pneumatic valves, shock absorbers, manometers, and so on.

Answer: $\tau = \sqrt{m/K}, \quad \zeta = \alpha\mu/2\sqrt{Km}$

1.7$_3$. Mass Transfer in Bubble Column

Bubble columns are used for liquid aeration and gas–liquid reactions. Thus, finely suspended bubbles produce large interfacial areas for effective mass transfer, where the contact area per unit volume of emulsion is calculated from the expression $a = 6\varepsilon/d_B$, where ε is the volume fraction of injected gas. While simple to design and construct, bubble columns sustain rather large eddy dispersion coefficients, and this must be accounted for in the modeling process. For concurrent operation, liquid of superficial velocity u_{0L} is injected in parallel with gas superficial velocity u_{0G}. The liquid velocity profile can be taken as plug shaped, and the gas voidage can be treated as uniform throughout the column. We wish to model a column used to aerate water, such that liquid enters with a composition C_0. Axial dispersion can be modeled using a Fickian-like relationship

$$J = -D_e \frac{dC}{dx} \quad \left(\frac{\text{moles}}{\text{liquid area} - \text{time}}\right)$$

while the solubility of dissolved oxygen is denoted as C^*. We shall denote distance from the bottom of the column as x.

(a) Derive the steady-state oxygen mole balance for an incremental volume of $A\Delta x$ (A being the column cross-sectional area) and show that the liquid phase balance is

$$(1 - \varepsilon)D_e \frac{d^2C}{dx^2} - u_{0L} \frac{dC}{dx} + k_c a(C^* - C) = 0$$

(b) Lump parameters by defining a new dimensionless length as

$$z = \frac{k_c a x}{u_{0L}}$$

and define the excess concentration as $y = (C - C^*)$, and so obtain the elementary, second-order, ordinary differential equation

$$\alpha \frac{d^2 y}{dz^2} - \frac{dy}{dz} - y = 0$$

where

$$\alpha = \frac{(1-\varepsilon) D_e k_c a}{u_{0L}^2} \quad \text{(dimensionless)}$$

Note the usual conditions in practice are such that $\alpha \leq 1$.

(c) Perform a material balance at the entrance to the column as follows. Far upstream, the transport of solute is mainly by convection: $A u_{0L} C_0$. At the column entrance ($x = 0$), two modes of transport are present; hence, show that one of the boundary conditions should be

$$u_{0L} C_0 = -(1-\varepsilon) D_e \left. \frac{dC}{dx} \right|_{x=0} + u_{0L} C(0)$$

The second necessary boundary condition is usually taken to be

$$\frac{dC}{dx} = 0 \quad \text{at} \quad x = L$$

where L denotes the position of the liquid exit. What is the physical meaning of this condition? The two boundary conditions are often referred as the Danckwerts type, in honor of P. V. Danckwerts.

1.8$_3$. Dissolution and Reaction of Gas in Liquids

Oxygen dissolves into and reacts irreversibly with aqueous sodium sulfite solutions. If the gas solubility is denoted as C_A^* at the liquid–gas interface, derive the elementary differential equation to describe the steady-state composition profiles of oxygen in the liquid phase when the rate of oxygen reaction is represented by $R_A = k C_A^n$ and the local oxygen diffusion flux is described by $J_A = -D_A \, dC_A/dz$, where D_A is diffusivity and z is distance from the interface into the liquid.

$$\text{Answer: } D_A \frac{d^2 C_A}{dz^2} - k C_A^n = 0$$

1.9$_3$. Modeling of a Catalytic Chemical Reactor

Your task as a design engineer in a chemical company is to model a fixed bed reactor packed with the company proprietary catalyst of spherical shape. The catalyst is specific for the removal of a toxic gas at very low concentration in air, and the information provided from the catalytic division is that the reaction is first order with respect to the toxic gas concentration. The reaction rate has units of moles of toxic gas removed per mass of catalyst per time.

The reaction is new and the rate constant is nonstandard, that is, its value does not fall into the range of values known to your group of design engineers. Your first attempt, therefore, is to model the reactor in the simplest possible way so that you can develop some intuition about the system before any further modeling attempts are made to describe it exactly.

(a) For simplicity, assume that there is no appreciable diffusion inside the catalyst and that diffusion along the axial direction is negligible. An isothermal condition is also assumed (this assumption is known to be invalid when the reaction is very fast and the heat of reaction is high). The coordinate z is measured from entrance of the packed bed. Perform the mass balance around a thin shell at the position z with the shell thickness of Δz and show that in the limit of the shell thickness approaching zero the following relation is obtained:

$$u_0 \frac{dC}{dz} = -(1-\varepsilon)\rho_p (kC)$$

where u_0 is the superficial velocity, C is the toxic gas concentration, ε is the bed porosity, ρ_p is the catalyst density, and (kC) is the chemical reaction rate per unit catalyst mass.

(b) Show that this lumped parameter model has the solution

$$\ln\left(\frac{C}{C_0}\right) = -\frac{(1-\varepsilon)\rho_p k}{u_0} z$$

where C_0 denotes the entrance condition.

(c) The solution given in part (b) yields the distribution of the toxic gas concentration along the length of the reactor. Note the exponential decline of the concentration. Show that the toxic concentration at the exit, which is required to calculate the conversion, is

$$C_L = C_0 \exp\left[-\frac{(1-\varepsilon)\rho_p k L}{u_0}\right]$$

(d) In reactor design, the information normally provided is throughput and mass of catalyst. So if you multiply the denominator and numerator of the bracketed term in the last part by the cross-sectional area, *A*, show that the exit concentration is

$$C_L = C_0 \exp\left[-\frac{Wk}{F}\right]$$

where *W* is the mass of catalyst and *F* is the volumetric gas flow rate.

(e) The dimensionless argument *Wk*/*F* is a key design parameter. To achieve a 95% conversion, where the conversion is defined as

$$X = \frac{C_0 - C_L}{C_0}$$

show that the nondimensional group *Wk*/*F* must be equal to 3. This means that if the throughput is provided and the rate constant is known the mass of catalyst required is simply calculated as

$$W = 3\frac{F}{k}$$

(f) The elementary Model 1 is of the lumped parameter type, and its validity is questionable because of a number of assumptions posed. To check its validity, you wish to relax one of the assumptions and move one level up the hierarchy ladder. Suppose, you relax the axial diffusion assumption, and hence show that the mass balance, when diffusion is important, becomes

$$D\varepsilon\frac{d^2C}{dz^2} - u_0\frac{dC}{dz} - (1-\varepsilon)\rho_p kC = 0$$

Since this is a second-order ordinary differential equation, two boundary conditions must be required. The two possible conditions after Danckwerts are

$$z = 0;\quad u_0C_0 = u_0C|_{z=0} - D\varepsilon\left.\frac{dC}{dz}\right|_{z=0}$$

$$z = L;\quad \frac{dC}{dz} = 0$$

(g) Define the following nondimensional variables and parameters

$$y = \frac{C}{C_0};\quad x = \frac{z}{L};\quad Pe = \frac{u_0L}{D\varepsilon};\quad N = \frac{Wk}{F}$$

and show that the resulting modeling equations are

$$\frac{1}{Pe}\frac{d^2y}{dx^2} - \frac{dy}{dx} - Ny = 0$$

$$x = 0;\quad 1 = y|_{x=0} - \frac{1}{Pe}\left.\frac{dy}{dx}\right|_{x=0}\qquad x = 1;\quad \frac{dy}{dx} = 0$$

Compare this model (hereafter called Model 2) with Model 1 and show that the axial diffusion may be ignored when $Pe \gg 1$ (this can be accomplished several ways: by decreasing porosity ε or by reducing *D*, or by increasing velocity or length).

(h) To study the effect of the mass transfer inside the catalyst particle, we need to remove the assumption of no diffusion resistance inside the particle. This means that the mass balance within the particle must be linked with the external composition. To investigate this effect, we shall ignore the axial diffusion (which is usually small for packing made up of finely granulated solid) and the external film resistance surrounding the particle.

Set up a thin spherical shell (control volume) inside the particle, and show that the mass balance equation is

$$D_e\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_p}{\partial r}\right) - \rho_p kC_p = 0$$

where C_p is the toxic gas concentration within the particle, and D_e is the effective diffusivity and is defined as Fickian-like

$$J_p = -D_e\frac{\partial C_p}{\partial r}\quad\left\{\frac{\text{moles transported by diffusion}}{\text{cross-sectional area-time}}\right\}$$

and suitable boundary conditions for negligible film resistance and particle symmetry are

$$C_p(R) = C;\quad \partial C_p/\partial r = 0\quad \text{at}\quad r = 0$$

where *R* denotes particle radius.

(i) Next, set up the mass balance around the thin element spanning the whole column cross section (as in Model 1), but this time the control volume will exclude the catalyst volume. This means that material is lost to the various sinks made up by the particles. Show that the mass balance equation on this new control volume is

$$-u_0\frac{dC}{dz} = (1-\varepsilon)\frac{3}{R}D_e\left.\frac{\partial C_p}{\partial r}\right|_{r=R}$$

1.10$_2$ Dimensional Analysis of a Correlation

As a follow up to Problem 1.7 on modeling bubble columns, we wish to find an expression to represent axial dispersion, sometimes called turbulent eddy mixing. Baird and Rice (1975) proposed an expression to account for the input power per unit mass, P_m, and the turbulent length scale or eddy size, δ, for the dispersion coefficient as follows:

$$D_e = cP_m^x(\delta)^y$$

The arbitrary constant c is seen to be dimensionless. We wish to find the dimensionally consistent values for the unknown exponents x and y. We will use the science of dimensional analysis to accomplish this task. First, write the units of length L and time t each term as follows:

$$\frac{L^2}{t} \equiv \left(\frac{L^2}{t^3}\right)^x L^y$$

We require the exponents for length on both sides of the equation to be the same, hence

$$L: 2 = 2x + y$$

Similarly for the exponents of time,

$$t: 1 = 3x.$$

(a) Solve the algebraic equations and show that

$$x = 1/3 \quad \text{and} \quad y = 4/3.$$

Baird and Rice took the pressure drop in the power calculation to be the hydrostatic head and the eddy size to be the column diameter (d), with the value of c fitted to a large array of experimental data. This widely cited expression for dispersion coefficient in terms of superficial gas velocity (U_{og}) and column diameter (d) is given as

$$D_e = 0.35(gU_{og})^{1/3}(d)^{4/3}$$

(b) The relations for the exponents x (call this x_1) and y (call this x_2) could have been represented using a vector–matrix format as follows:

$$\mathbf{b} = \mathbf{Ax}; \;\; \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}; \;\; \mathbf{b} = \begin{pmatrix} 2 \\ 1 \end{pmatrix}; \;\; \mathbf{A} = \begin{bmatrix} 2 & 1 \\ 3 & 0 \end{bmatrix}.$$

If we premultiply $\mathbf{b}$ by $\mathbf{A}^{-1}$, we obtain the expression for $\mathbf{x}$:

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

Find the elements of $\mathbf{A}^{-1}$ and solve for the elements of $\mathbf{x}$.

$$\text{Answer: } \begin{bmatrix} 0 & 1/3 \\ 1 & -2/3 \end{bmatrix} = A^{-1}$$

1.11$_2$ Transformations

Write the matrix form for the following linear equations:

$$\begin{aligned} y_1 &= \frac{1}{\sqrt{2}}x_1 + \frac{1}{\sqrt{2}}x_3 \\ y_2 &= x_2 \\ y_3 &= -\frac{1}{\sqrt{2}}x_1 + \frac{1}{\sqrt{2}}x_3 \end{aligned}$$

And show that

$$\boldsymbol{y} = \boldsymbol{Ax}; \text{ where } \boldsymbol{A} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{-1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}$$

(a) Compute the transpose of A^{-1} and compare it with the original matrix A.

(b) What is the geometric relation of x to y ?

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