

*To see a World in a Grain of Sand,
And a Heaven in a Wild Flower,
Hold Infinity in the palm of your hand,
And Eternity in an hour*

— WILLIAM BLAKE

Chapter 1

The physical, mathematical and computational models

1.1 Introduction

In the Trekie language, the *prime directive* of a chemical engineer should be explore and understand physical and chemical processes involved in converting a raw material into a useful product. Use this knowledge in designing, constructing and operating chemical process plants. This definition is as arbitrary as anything else that one might propose. In fact if one substitutes the word chemical in the above definition with any other (such a mechanical or electrical) it would remain equally valid. This is because the basic principles and the scientific methodology we use to uncover such principles remain the same in any field of engineering or science. A broader, although highly personal, view of the our attempt to understand the physical world, describe it in the language of mathematics, and finally investigate its consequence by means of analytical, graphics or numerical methods is shown in Figure 1.1.

A mathematical model is at best an approximation to the physical world. Such models are constructed based on certain conservation principles and/or empirical observations. Those curious about the nature of the physical laws should read a delightful little book by Feynman (1967) on the character of physical laws. As a matter of convenience mathematical models can be classified as *linear* or *non-linear*, *steady-state* or *dy-*

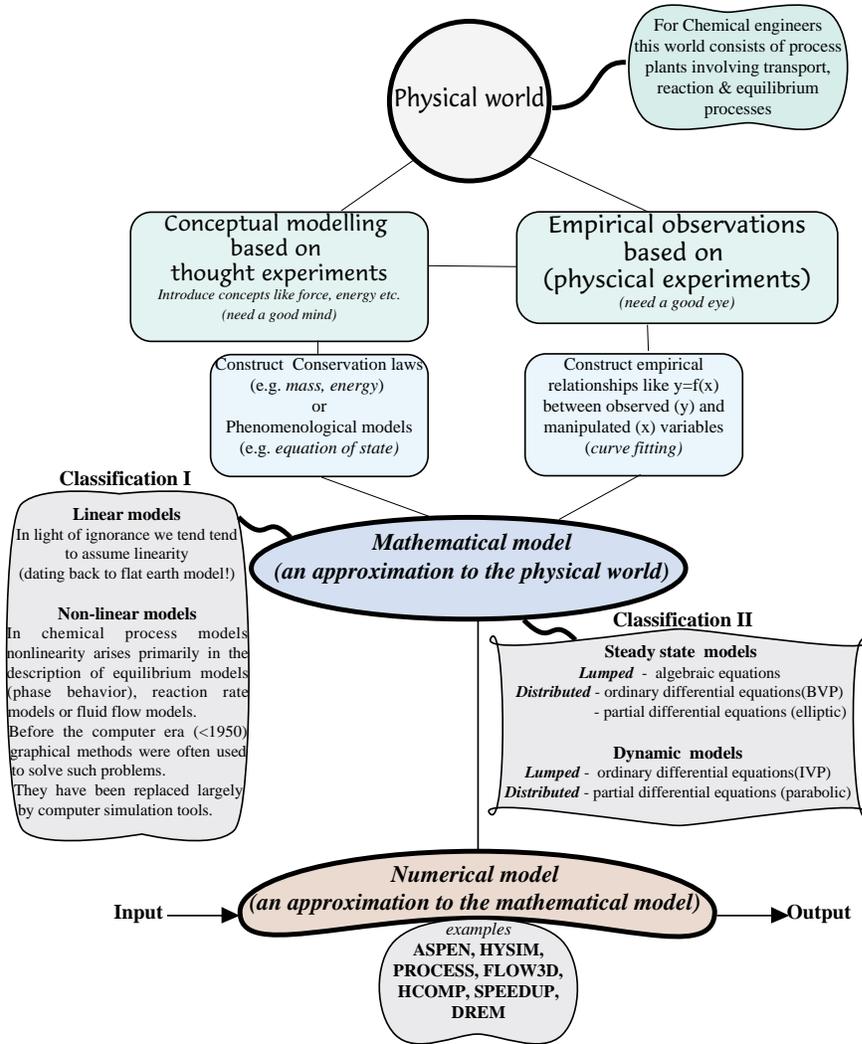


Figure 1.1: Scheme of things - a personal view

namic, lumped or distributed. Examples to illustrate each type of model are provided later in this chapter. In general, non-linearity is found to occur quite naturally and frequently in nature; it is also very difficult to analyse non-linear models without the aid of a computer.

A numerical model (or a computer simulation tool) is an approximation to the mathematical model. Although the importance of mathematical modelling in chemical engineering was recognized since the early 1920's, it was the text by Bird *et al.* (1960) on **Transport Phenomena** that has proved to be the major inspiration in exploring the link between the physical world and the mathematical one for *transport processes* involving momentum, heat and mass transfer. Since then a number of outstanding texts have appeared that explore this relationship for *reaction* and *equilibrium* processes as well. While such studies form the core of chemical engineering curriculum, the importance of sharpening our mathematical abilities, and the need to incorporate these as part of the curriculum was recognized and aided by the appearance of early text books by Amundson (1966) and Jenson & Jeffreys (1963). These dealt specifically with mathematical applications of chemical engineering. The texts by Lapidus (1962) and Rosenbrock (1966) served a similar purpose in introducing digital computational methods in the analysis of chemical processes.

We are now at a new threshold; computers have become quite pervasive. Significant advances have been made in our ability to analyse non-linear systems. The advances in both the hardware and software technology have been revolutionary. As a result of these advances, computer aided design and analysis has become a standard tool as evidenced by the success of several commercial packages such as ASPEN PLUS, PROCESS, HYSIM (steady state process simulators), FLOW3D, FLUENT (fluid dynamics simulators), HCOMP, DREM (multiphase and transient pipeline flow simulators) *etc.* In addition to such simulators that are specific for certain classes of problems, general purpose mathematical tools such as MATLAB (for matrix linear algebra functions), Mathematica and MAPLE (for symbolic computation) provide easy access to a vast array of mathematical functions and the ability to process them both symbolically and numerically. Such packaged tools tend to accomplish the following: (i) codify the most advanced algorithms, (ii) assemble a vast database (in the case of physical properties) and knowledge base in the case of mathematical functions (in MAPLE and Mathematica) and (iii) make these accessible to the end user through an intuitive interface. While this puts a lot of power at the hands of the end user, in order to use them wisely and interpret the results correctly, the users are expected to have a sound knowledge of the relationship between the physical world and the mathe-

mathematical model and that between the mathematical model and the numerical approximation. One is well served to remember the cliché *garbage in, garbage out!*

In this course we examine the link between the mathematical and the numerical model. In so doing modern computational tools are used quite liberally. Concepts of a networked computer environment are discussed in Appendix A. A basic introduction to MATLAB can be found in Appendix B. MATLAB is used throughout in illustrating various algorithms.

1.2 Classification of chemical process models

In modelling chemical processes, one is interested in tracking material and energy of process streams from the raw material stage to the finished product state. The *state of a stream* is characterized by the concentration of the various species that it carries and its temperature, pressure and flow rates. Applying the laws of conservation of mass, energy and momentum allows us to track changes in the state of the system. Typically we subject the raw material streams to either physical treatment to add or remove chemical species exploiting such property differences as density, solubility, volatility, diffusivity *etc.* (transport and equilibrium processes) or, chemical treatment to alter the chemical structure (reaction processes).

If the state variables are assumed to be independent of time and spatial position, then we often have a lumped parameter, steady state model resulting in a set of coupled algebraic equations. If they are assumed to have no spatial variation, but are time dependent, then we have lumped parameter, dynamic models which result in ordinary differential equations of the initial value type. If there is no time dependence, but there is a spatial variation and that too restricted to one dimension (for reasons of symmetry or scale), then we have ordinary differential equations of the boundary value type. If both spatial and time dependence are important, then we end up with partial differential equations, which are further classified into parabolic, elliptic and hyperbolic equations. The classification outlined in this paragraph are illustrated with specific examples in the next sections. The examples are drawn from *transport, equilibrium* and *reaction processes*. The objective is to sensitize you to the model building process in the hope that you would begin to appreciate the relationship between the physical world and the mathematical model that represents it.

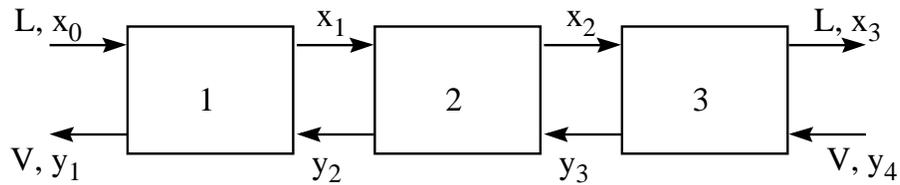


Figure 1.2: Three stage separation process

1.3 Lumped parameter, steady state models

1.3.1 Example of a stagewise separation process

Consider a stagewise separation process shown in Figure 1.2. Suppose we wish to process a gas stream at a rate of V kmole/s containing a pollutant at a mole fraction of y_4 . We wish to remove the pollutant by scrubbing it with a solvent in a counter-current 3-stage separation device. The liquid rate is, say, L kmole/s and it contains a pollutant concentration of x_0 (which may be zero for a pure solvent stream). Only the pollutant transfers from the gas phase to the liquid phase and we make use of the solubility differences between the inert carrier gas and the pollutant. So far we have made an attempt to describe a physical world. Is the description adequate to formulate a mathematical model? How do we know that such a model should result in a steady state, lumped parameter model? The answer is no, we don't! We need to further define and refine the problem statement. For a process engineer this is the most important step - viz. understand the objective of the task and the nature of the process (the physical world) to formulate a mathematical model. Let us continue with the description of the problem.

The state variables in this problem are $(L, V, x_0, x_1, x_2, x_3, y_1, y_2, y_3, y_4)$. By focusing only the steady state operation, we remove the dependence of state variables on time. Such a model cannot clearly answer any questions concerning start up or shutdown of this process. Next, we assume that in each stage the gas and liquid are mixed thoroughly so that there is no spatial variation of concentration within the equipment. This is the so-called lumped parameter approximation.

We further assume that the streams leaving a stage are in thermodynamic equilibrium. This implies that for a given inlet streams, *no matter what we do inside the process equipment*, the exit concentrations cannot be changed as they have reached an invariant state. To state it another way, there is a unique relationship, $y = f(x)$, between the exit concen-

trations of each stage and this relationship could be determined in a laboratory and entered into a database. Often this relation is expressed as, $y = Kx$ where K is called the equilibrium ratio; at extremely low concentration range K may be assumed to be a constant (results in a linear model), while at higher concentrations the equilibrium ratio may itself be a function of concentration, $K(x)$ (results in a non-linear model). While experience and experimentation suggest that such relationships do exist, study of equilibrium thermodynamics takes this one step further in attempting to construct predictive models for the function, $y = f(x)$ by examining the equilibrium process at a molecular level. Let us continue with the assumption that the equilibrium model is given by

$$y_n = Kx_n \quad n = 1, 2, 3 \quad (1.1)$$

where we have introduced the subscript n to indicate the equilibrium relationship is valid for each stage of the separation process. This yields us three equations, but recall that the state of this 3-stage separation train is described by 10 variables: $(L, V, x_0, x_1, x_2, x_3, y_1, y_2, y_3, y_4)$. At this stage we ask ourselves if there are other laws or principles that this system should obey. Conservation laws such as mass, momentum and energy conservation should come to mind. In the present case our objective has been narrowly focused on tracking the concentration of the pollutant in each of the three stages. In particular we have not concerned ourselves with flow and heat effects. Let us speculate briefly what these effects might be! Heat transfer effects might include heat of absorption, while flow effects will include imperfect mixing in a stage. The later in fact has serious consequence in negating two of our earlier assumptions: viz. lumped parameter system implying concentration is spatially uniform in each stage and the exit streams are in thermodynamic equilibrium. Nevertheless, we still proceed with the assumption of perfect mixing; a model description that takes into accounts such realities often becomes intractable. Neglecting heat and flow effects, we have only mass conservation principle. Applying this for the pollutant species around each of the three stages, we obtain,

$$\begin{aligned} \text{Stage 1:} & \quad V(y_2 - y_1) = L(x_1 - x_0) \\ \text{Stage 2:} & \quad V(y_3 - y_2) = L(x_2 - x_1) \\ \text{Stage 3:} & \quad V(y_4 - y_3) = L(x_3 - x_2) \end{aligned} \quad (1.2)$$

Note that in each of these equations, the left hand side represents the amount of pollutant that has been removed from the gas phase and the right hand side represents the same amount of material absorbed into

the liquid phase. Now we have a total of six equations, but still ten variables. Hence we conclude that we have four degrees of freedom. This implies that we can choose four of the variables and the remaining six variables must be determined by satisfying the six equations.

One can also write an overall balance, taking all three stages as one group:

$$\text{Overall:} \quad V(y_4 - y_1) = L(x_3 - x_0) \quad (1.3)$$

This, however, is not an independent equation since summing equations (1.2) produces equation (1.3). This will be used later in introducing concepts of linear independence and rank of matrices.

Specifications: a 3-stage linear system

Let us assume that we pick the four variables associated with the inlet streams to be specified, viz. (L, V, x_0, y_4) . Defining $S = L/KV$ (a known value) and eliminating variables (y_1, y_2, y_3) from equations (1.2) we get the following system of three equations

$$\begin{bmatrix} (1+S) & -1 & 0 \\ -S & (1+S) & -1 \\ 0 & -S & (1+S) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} Sx_0 \\ 0 \\ y_4/K \end{bmatrix} \quad (1.4)$$

in the unknowns (x_1, x_2, x_3) . This can be represented in compact matrix form as

$$\mathbf{T}\mathbf{x} = \mathbf{b} \quad (1.5)$$

where \mathbf{T} represents the *tridiagonal matrix*

$$\mathbf{T} = \begin{bmatrix} d_1 & c_1 & 0 \\ a_1 & d_2 & c_2 \\ 0 & a_2 & d_3 \end{bmatrix} = \begin{bmatrix} (1+S) & -1 & 0 \\ -S & (1+S) & -1 \\ 0 & -S & (1+S) \end{bmatrix}$$

and

$$\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} Sx_0 \\ 0 \\ y_4/K \end{bmatrix}$$

First variation: n-stage separation sequence

Once we have expressed the mathematical model in a symbolic, matrix form as in equation (1.5), we can generalize the model to any number of

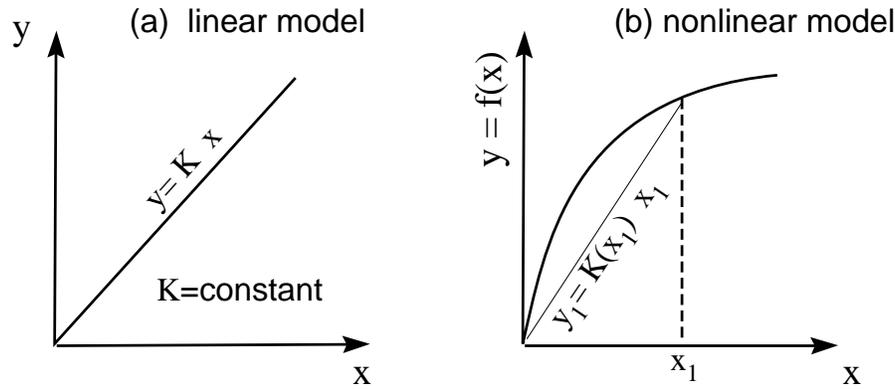


Figure 1.3: Linear and nonlinear equilibrium model

stages. Suppose there are n stages, then we merely have,

$$T = \begin{bmatrix} d_1 & c_1 & 0 & \cdots & 0 \\ a_1 & d_2 & c_2 & \cdots & 0 \\ & & \ddots & & \\ 0 & 0 & a_{n-2} & d_{n-1} & c_{n-1} \\ 0 & \cdots & 0 & a_{n-1} & d_n \end{bmatrix} \quad \mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_{n-1} \\ x_n \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_{n-1} \\ b_n \end{bmatrix}$$

where $a_i = -S$, $d_i = (1 + S)$, $c_i = -1$. Efficient algorithms for solving such system will be developed in Chapter 3.

Second variation: nonlinear equilibrium model

Instead of assuming the equilibrium ratios, K in equation (1.1) to be constant as in figure 1.3a, if they are found to be dependent on concentrations x , then we have a nonlinear system of equations. One can then interpret the $K(x)$ values to be the slopes of the chord as shown in figure 1.3b, which is no longer a constant, but depends on x . This implies that, $S(x) = L/K(x)V$ and hence T becomes a function of \mathbf{x} . Thus the elements in T cannot be determined without knowing the solution \mathbf{x} . An intuitive approach to resolving this dilemma in solving such systems, $T(\mathbf{x})\mathbf{x} = \mathbf{b}$ might be to make an initial guess for \mathbf{x}^{old} and use this guess to evaluate, $K(\mathbf{x}^{old})$, $S(\mathbf{x}^{old})$ and hence $T(\mathbf{x}^{old})$ and obtain a new solution for \mathbf{x}^{new} by solving the *linearized system*, $T(\mathbf{x}^{old})\mathbf{x}^{new} = \mathbf{b}$. One can repeat this procedure until the difference between the new and the old values of \mathbf{x} becomes vanishingly small. Although there are numerous variations on this scheme, a large class of non-linear problems are

solved within the conceptual frame work (i) estimating an initial guess (ii) devising an algorithm to improve the estimate and (iii) checking for convergence of the result.

Third variation: alternate specification

In all of the previous cases we considered the inlet streams to be specified viz. (L, V, x_0, y_4) . This would be typical for performance analysis problems where the output of an existing process is desired, given its inlet conditions. A design engineer, who gets into this game at an earlier stage, might face an alternate problem. For example, environmental regulations might dictate that the exit concentration of the pollutant y_1 be below a certain acceptable level. Thus the four degrees of freedom might be used up in specifying (V, x_0, y_4, y_1) . Assuming once again a linear equilibrium model (K constant), the system of equations (1.2) in the unknown set (L, x_2, x_3) can be written as:

$$\begin{aligned} f_1(L, x_2; V, y_1, x_0) &:= V(Kx_2 - y_1) - L(y_1/K - x_0) = 0 \\ f_2(L, x_2, x_3; V, y_1, x_0) &:= KV(x_3 - x_2) - L(x_2 - y_1/K) = 0 \\ f_3(L, x_2, x_3; V, y_4) &:= V(y_4 - Kx_3) - L(x_3 - x_2) = 0 \end{aligned} \quad (1.6)$$

In spite of assuming a linear equilibrium model, the above set of equations are non-linear! Why? Although the mathematical model has remained the same for various specifications, we have nice tridiagonal matrix structure for some specifications while no such structure exists for others.

1.3.2 Process flow sheet simulation

Consider the flow sheet shown in figure 1.4. It is an extremely simple unit consisting of a reactor and a separator. We are given the mole fractions of components in the recycle stream and the exit stream from the reactor. We are asked to determine the molar rates of CO and H_2 in the inlet stream, the recycle rate R and the product rate, P . In analysing this problem we setup a series of material balance equations. Focusing on the reactor loop (loop 1) shown in dashed line in figure 1.4, we can write the following three component material balance equations:

$$\text{C-balance: } x + R(0.302 + 0.004) = (0.274 + 0.095) \times 275$$

or

$$x + 0.306R = 101.475$$

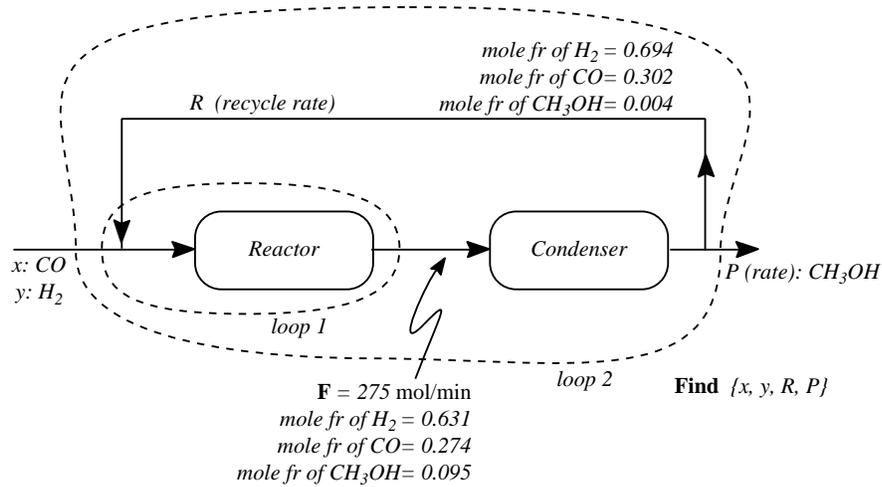


Figure 1.4: Example of material balance equations in a process flow sheet.

$$\text{H}_2\text{-balance: } y + R(0.694 + 0.008) = (0.631 + 2 \times 0.095) \times 275$$

or

$$y + 0.702R = 225.775$$

$$\text{O-balance: } x + R(0.302 + 0.004) = (0.274 + 0.095) \times 275$$

or

$$x + 0.306R = 101.475$$

Note that the O balance equation is redundant and in the language of linear algebra, these three equations do not form a *linearly independent* set of equations. So we proceed to construct additional equations by examining material balance around the full flow sheet (loop 2). These give rise to:

$$\text{C-balance: } x = P$$

$$\text{H}_2\text{-balance: } y = 2P$$

These five equations can be arranged in a matrix form as,

$$\begin{bmatrix} 1 & 0 & 0.306 & 0 \\ 0 & 1 & 0.702 & 0 \\ 1 & 0 & 0.306 & 0 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 0 & -2 \end{bmatrix} \begin{bmatrix} x \\ y \\ R \\ P \end{bmatrix} = \begin{bmatrix} 101.475 \\ 225.775 \\ 101.475 \\ 0 \\ 0 \end{bmatrix} \quad (1.7)$$

Recognizing the redundancy between the first and third equations and also combining equations four and five to eliminate P , we can write the above set in an alternate form as

$$\begin{bmatrix} 1 & 0 & 0.306 \\ 0 & 1 & 0.702 \\ -2 & 1 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ R \end{bmatrix} = \begin{bmatrix} 101.475 \\ 225.775 \\ 0 \end{bmatrix} \quad (1.8)$$

1.3.3 Example of a multicomponent flash

Next, we examine a model for a multicomponent, isothermal flash process. This also results in a lumped, steady state model description. It is also an example of how a potentially large system system of algebraic equations can be reduced to a single equation in one unknown through clever manipulations. Thus root finding algorithms could be used efficiently to solve this system. A sketch of the process is shown in figure 1.5. A feed stream of known flow rate, F , composition (mole fractions), $\{z_i | i = 1 \dots N\}$, temperature, T_F and pressure, P_F is flashed into a drum maintained at a temperature and pressure of (T, P) , respectively. Under right conditions, the feed will split into a vapor phase and a liquid phase. The objective is to predict the flow rate and compositions of the vapor, (V, y_i) and the liquid (L, x_i) phases. Each exit stream contains $(N + 1)$ unknowns. The assumptions are that the process is operating under steady conditions, perfect mixing takes place inside the drum (lumped approximation) and the exit streams are in thermodynamic equilibrium. The model equations are as follows:

Thermodynamic equilibrium - (empirical model)

$$y_i = K_i(T, P)x_i \quad i = 1 \dots N \quad (1.9)$$

Component material balance - (mass conservation)

$$Fz_i = Vy_i + Lx_i \quad i = 1 \dots N \quad (1.10)$$

Observe the nonlinear terms in this equation: viz. product of unknowns V & y_i and L & x_i

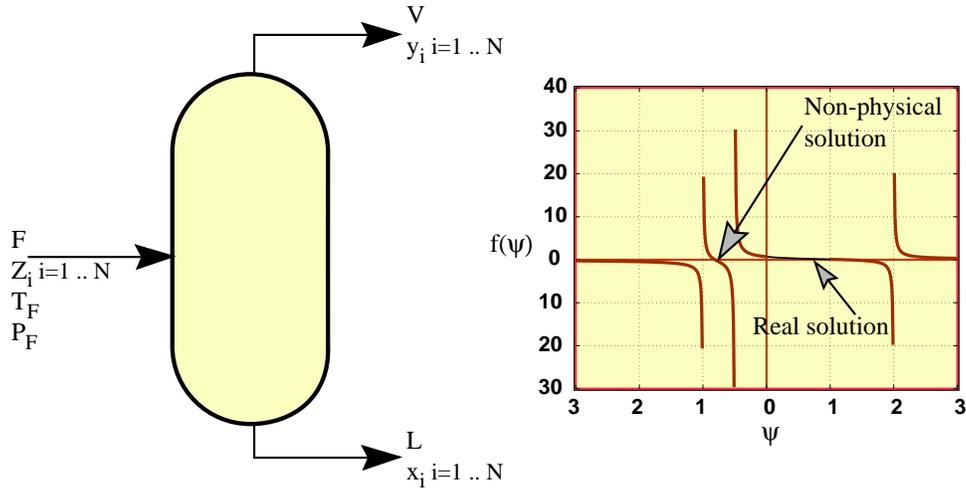


Figure 1.5: Multicomponent, isothermal flash process

Overall material balance

$$F = V + L \quad (1.11)$$

Mole fraction constraints

$$\sum_i^N y_i = \sum_i^N x_i = 1 \quad (1.12)$$

A simple count indicates that we have written down $(2N + 3)$ equations for the $(2N + 2)$ unknowns; but it is easy to verify that summing equations (1.10) over all components and using the mole fraction constraint, results in equation (1.11). Thus, equation (1.11) is not an independent one. Although these equations could be solved as a system of nonlinear algebraic equations, a much more efficient scheme is to eliminate all, except one variable and reduce the system into a single equation. First eliminate y_i from equation (1.10) using (1.9) to obtain

$$Fz_i = (K_iV + L)x_i \quad \text{or} \quad x_i = Fz_i/(K_iV + L)$$

Rearrange equation (1.12) as,

$$\sum_i^N (x_i - y_i) = 0 \quad \text{or} \quad \sum_i^N (1 - K_i)x_i = 0$$

Combine the last two equations as,

$$\sum_i^N \frac{(1 - K_i)Fz_i}{K_iV + L} = 0$$

Eliminate L from above equation using (1.11) and define $\psi = V/F$ to get the final form of the flash equation as.

$$\boxed{\sum_i^N \frac{(1 - K_i)z_i}{(K_i - 1)\psi + 1} = 0} \quad (1.13)$$

This is a single equation in one unknown, viz. ψ . In general the number of roots that a nonlinear equation possesses cannot be known *a priori*. A possible sketch of the function is shown in figure 1.5b. Since ψ is defined as the fraction of feed that appears as vapor, (V/F), the physical world dictates that it must lie between (0, 1) and it is sufficient if the search for the root is limited to this range. The flash equation (1.13) may possess other roots outside the range of interest (0, 1). Such roots are valid mathematical solutions of the problem, they are not physically relevant.

1.3.4 Example of a phenomenological model

In the previous two examples, models were built based on conservation laws. Models based on empirical observations are also quite common. The Pressure-Volume-Temperature (PVT) behavior of gases, for example, could be modeled by the *ideal gas law* viz. $PV = nRT$. A more refined model, called the Peng-Robinson equation of state is used widely in chemical engineering literature. It is given by the following equations:

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (1.14)$$

where

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T_r, \omega)$$

$$b = 0.0778 \frac{RT_c}{P_c}$$

$$\alpha^{1/2} = 1 + m(1 - \sqrt{T_r})$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Here T_c, P_c are the critical temperature and pressure of the component and ω is the acentric factor. These are properties of a component.

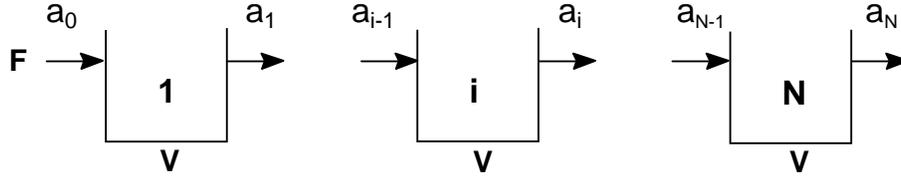


Figure 1.6: Reactors in series

We define $T_r = T/T_c$ as the reduced temperature, and $Z = PV/RT$ as the compressibility factor. Equation (1.14) can be rearranged as a cubic equation in Z as follows:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (1.15)$$

where $A = aP/R^2T^2$ and $B = bP/RT$. For the class of problems where the pressure and temperature (P, T) are given and the material is identified (*i.e.*, T_c, P_c, ω are known), the coefficients (A, B) in equation (1.15) can be calculated and hence the cubic equation can be solved to find the roots, Z . This allows the determination of the volume (or density) from $Z = PV/RT$.

1.3.5 Example of reactors in series

An example from chemical reaction engineering process that gives rise to a system of nonlinear equations is that of a continuously stirred tank reactor in series. A sketch is shown in figure 1.6 Consider an isothermal, irreversible second order reaction. The composition in each reactor is assumed to be spatially homogeneous due to thorough mixing. The reaction rate expression is given by,

$$r = kVa_i^2$$

where a_i is the exit concentration of component A from the i -th reactor, k is the reaction rate constant and V is the volume of the reactor. A material balance under steady state conditions on the i -th reactor results in,

$$kVa_i^2 = F(a_{i-1} - a_i) \quad (1.16)$$

Letting $\beta = kV/F$, we have the following n-simultaneous nonlinear equations.

$$f_i := \beta a_i^2 + a_i - a_{i-1} = 0 \quad i = 1 \cdots N \quad (1.17)$$

While we have constructed N equations, there are $(N + 2)$ variables in total. They are $[a_0 \cdots a_N \beta]$. Hence we have two degrees of freedom. In analysing an existing reactor train, for example, one might regard (β, a_0) to be known and solve for the remaining N variables including the exit concentration a_N (and hence the conversion). In a design situation one might wish to achieve a specific conversion and hence regards (a_0, a_N) as knowns and solve for remaining N variables including β (and hence the volume V).

1.4 Lumped parameter, dynamic models

Lumped parameter, dynamic models arise typically when the spatial variation of the state variables can be ignored for some reason, but time variation cannot be ignored. Let us consider an example from heat transfer.

1.4.1 Example of cooling a molten metal

A sample of molten metal at an initial temperature of T_i is placed in a crucible (at an initial temperature of T_∞) and allowed to cool by convection. A sketch is shown in figure 1.7. Let $T_1(t)$ be the temperature of the molten metal at any time t and $T_2(t)$ be the temperature of the crucible. The argument used to justify neglecting spatial variation is that the thermal conductivity of the two materials are sufficiently large to keep the temperature of each material uniform within its boundaries. The conservation law statement is:

$$\{\text{rate of accumulation}\} = \{\text{rate in}\} - \{\text{rate out}\} + \{\text{rate of generation}\}$$

Applying this first to the molten metal,

$$\frac{d}{dt}(m_1 C_{p1} T_1) = \underbrace{-h_1 A_1 (T_1 - T_2)}_{\text{heat loss from 1 to 2}} \quad (1.18)$$

Energy balance on the crucible results in,

$$\frac{d}{dt}(m_2 C_{p2} T_2) = \underbrace{h_1 A_1 (T_1 - T_2)}_{\text{heat gain by 2 from 1}} - \underbrace{h_2 A_2 (T_2 - T_\infty)}_{\text{heat loss from 2 to } \infty} \quad (1.19)$$

These two equations can be presented using matrix notation as follows:

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

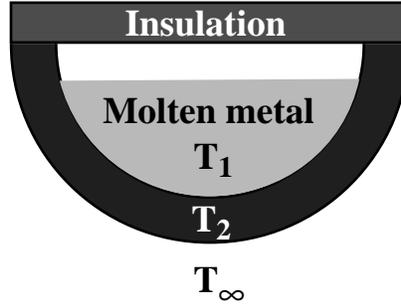


Figure 1.7: Heat transfer from a molten metal

where

$$\underline{\theta} = \begin{bmatrix} T_1 \\ T_2 \end{bmatrix} \quad \mathbf{A} = \begin{bmatrix} -\frac{h_1 A_1}{m_1 C_{p1}} & \frac{h_1 A_1}{m_1 C_{p1}} \\ +\frac{h_1 A_1}{m_2 C_{p2}} & -\frac{h_1 A_1 + h_2 A_2}{m_2 C_{p2}} \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} 0 \\ \frac{h_2 A_2 T_\infty}{m_2 C_{p2}} \end{bmatrix}$$

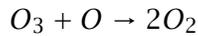
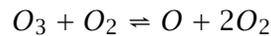
The initial condition is

$$\underline{\theta}(t = 0) = \begin{bmatrix} T_i \\ T_\infty \end{bmatrix}$$

This problem depends on several parameters which are assumed to be known. A_1 is the heat transfer area at the metal-crucible interface, A_2 is the area at the crucible-air interface. (h_1, h_2) are the corresponding heat transfer coefficients, (m_1, m_2) are the corresponding mass of the materials, (C_{p1}, C_{p2}) are the specific heats of the two materials. Since all of these are assumed to be known constants, the problem is linear.

1.4.2 Ozone decomposition

A number of mechanisms (some involving 40 steps and 40 equations) have been proposed to model the decomposition of ozone in the atmosphere. Let us consider a simple two-step model.



In the early stages of research, we were mainly concerned with identifying the mechanisms of ozone depletion in the atmosphere. For lack of better data, the compositions were assumed to be spatially homogeneous in the atmosphere, although we know now that there can be spatial variations. For the present purpose we will assume the compositions to be spatially uniform. Let y_1 be the composition of O_3 and y_2 be that of O . The model equations are,

$$\frac{dy_1}{dt} = f_1(y_1, y_2) = -y_1 - y_1 y_2 + \epsilon \kappa y_2 \quad (1.20)$$

$$\epsilon \frac{dy_2}{dt} = f_2(y_1, y_2) = y_1 - y_1 y_2 - \epsilon \kappa y_2 \quad (1.21)$$

The initial compositions are $\underline{y}(t = 0) = [1.0, 0.0]$. The parameters are $\epsilon = 1/98$ and $\kappa = 3.0$. This is a system of two non-linear ordinary differential equations. It is an interesting problem in the limit of $\epsilon \rightarrow 0$. In the reaction analysis literature, the consequence of this limit is known as the *quasi-steady-state-approximation*. The physical interpretation is that the second reaction is much faster than the first one so that it can be assumed to have reached the equilibrium state at every instant of time. The second equation becomes an algebraic one. In the applied mathematics literature it is called the *singular perturbation* problem. From the computational point of view this limit gives rise to a phenomena called *stiff systems*. We will explore these features further in later chapters.

1.5 Distributed parameter, steady state models

1.5.1 Heat transfer through a tapered fin

Let us examine an example from *transport processes*. Consider the use of a fin to enhance the rate of heat transfer. Basically, a fin provides a large heat transfer surface in a compact design. In the design and performance analysis of fins one might be interested in a variety of questions such as what is the efficiency of the fin? (as a corollary what is a useful definition of fin efficiency?), How many fins are required to dissipate a certain heat load?, What is the optimal shape of the fin that maximizes the heat dissipation for minimum weight of fin material? How long does it take for the fin to reach a steady state? *etc.* You will learn to develop answers to these questions in a heat transfer course. Our interest at this stage is to develop a feel for the model building process. A sketch of a fin is shown in figure 1.8. Let us first examine the steady state behavior

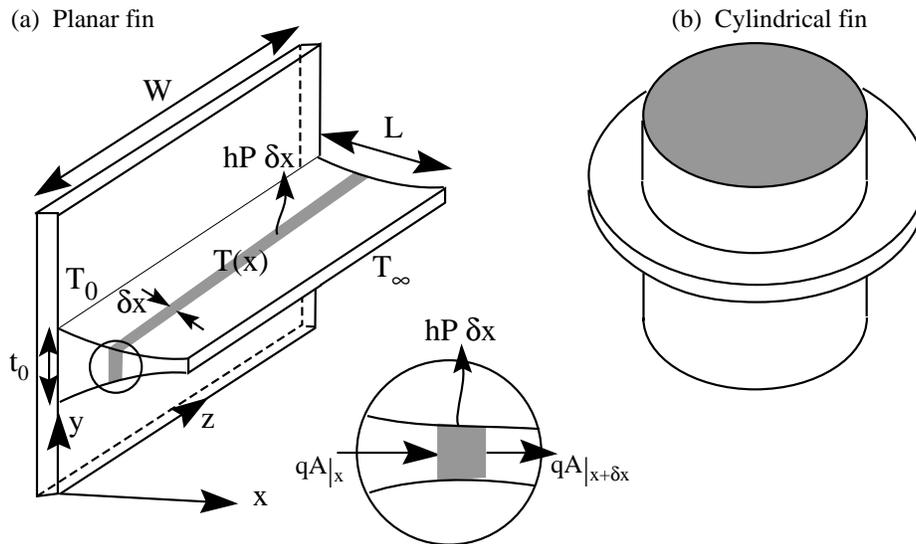


Figure 1.8: Heat transfer through a fin

of a planar fin shown in figure 1.8a. The base of the fin is maintained at a uniform temperature of T_0 and the ambient temperature is T_∞ . The state variable that we are interested in predicting is the temperature of the fin, T . In general it might be a function of all three spatial positions *i.e.*, $T(x, y, z)$. (Note time, t is eliminated by assuming steady state). If we know something about the length scales of the fin and the material property of the fin, we make further assumptions that will reduce the complexity of the problem. Let us also assume that the fin is made of a homogeneous material *i.e.*, its thermal conductivity, k is independent of position. If the length, L , of the fin is much larger than the thickness, t_0 , then we might argue that the temperature variation in the y direction will be smaller than that in the x direction. Thus we can assume T to be uniform in the y direction. Next, we examine what happens in the z direction? This argument is somewhat subtle as it is based on symmetries in the system. The basic premise here is that symmetric causes produce symmetric effects. An excellent and easily accessible exposition on this topic can be found in Golubiksky and Stewart (1993). First we assume that the ends of the fin in the z direction are at infinity (or $W \gg L$) so that the end effects can be neglected. Since the temperature gradient within the fin is caused by the driving force T_0 and T_∞ which are independent of z direction, we can expect the fin to respond in a

What types of materials might violate this assumption?

similar way - viz. T to be independent of z . Note that the end effect, however small it may be, is always present in a planar fin. By making W large compared to L we reduce the error caused by the two-dimensional effect near the ends. On the other hand the azimuthal symmetry in the circular fin (figure 1.8b) make the problem truly one dimensional with temperature varying only in the radial direction. Now that we have a better feel for what kinds of arguments or assumptions make this problem one-dimensional, let us proceed with constructing the model equation.

Since the temperature variation is present only in the x direction, we take an elemental control volume of thickness δx and identify the input and output sources of energy into this control volume. See figure 1.8. Energy enters by conduction mechanism at a rate of $(qA)|_x$ through the left boundary at x and leaves at a rate of $(qA)|_{x+\delta x}$ through the right boundary at $x + \delta x$. Heat is also lost by convection through the upper and lower boundaries, which is represented by $hP\delta x(T - T_\infty)$. Here q is the heat flux ($J/s \cdot m^2$) by conduction. This is given by another phenomenological model called the Fourier law: $q = -k \frac{dT}{dx}$. k in the Fourier law defines a material property called thermal conductivity ($J/m \cdot s \cdot ^\circ C$). A is the cross-sectional area which is allowed to be a function of x (tapered fin), h is the heat transfer coefficient ($J/s \cdot m^2 \cdot ^\circ C$). $P = 2W$ is the perimeter (m). The conservation law statement is:

$$\{\text{rate of accumulation}\} = \{\text{rate in}\} - \{\text{rate out}\} + \{\text{rate of generation}\}$$

In symbolic terms, it is given by,

$$0 = (qA)|_x - (qA)|_{x+\delta x} - hP\delta x(T - T_\infty)$$

Dividing by δx and taking the limit of $\delta x \rightarrow 0$, we obtain,

$$0 = -\frac{d(qA)}{dx} - hP(T - T_\infty)$$

Using the Fourier law to replace q in terms of T ,

$$\boxed{\frac{d}{dx} \left[kA \frac{dT}{dx} \right] - hP(T - T_\infty) = 0} \quad (1.22)$$

Equation (1.22) is a second order ordinary differential equation. The physical description dictates that two conditions be specified at the two ends of the fin, viz.

$$\begin{aligned} T(x=0) &= T_0 \\ T(x=L) &= T_\infty \\ \left. \frac{dT}{dx} \right|_{x=L} &= 0 \end{aligned} \quad (1.23)$$

This problem can be solved to obtain $T(x)$ provided the geometrical parameters $\{A(x), P\}$, the material property, k and the heat transfer environment $\{h, T_\infty, T_o\}$ are known. The problem is nonlinear if the thermal conductivity is a function of temperature, $k(T)$. In order to determine the effectiveness of the fin, one is interested in the total rate of heat transfer, Q through the fin. This is can be computed in one of two ways as given by,

$$Q = \int_0^L hP[T(x) - T_\infty] dx = -k \left. \frac{dT}{dx} \right|_{x=0} \cdot A(x=0)$$

1.6 Distributed parameter, dynamic models

1.6.1 Heat transfer through a tapered fin

As an example of a distributed, dynamic model let us re-examine the fin problem, but during the early transient phase. Let the fin be initially at the uniform ambient temperature of T_∞ . At time $t = 0$ suppose the base of the fin at $x = 0$ is brought to a temperature of T_o . One might ask questions like, how long will it take for the fin to reach a steady state? what will be the temperature at the tip of the fin at a given time? *etc.* Now we have the temperature as a function of both position and time, *i.e.*, $T(x, t)$. We can represent the rate of accumulation within a control volume symbolically as, $\frac{d(\rho A \delta x C_p T)}{dt}$ where the term in parenthesis is the energy (J) at any time within the control volume, C_p is the specific heat of the fin material ($J/kg \cdot ^\circ C$) and ρ is the density of the material. Thus the transient energy balance becomes,

$$\frac{\partial(\rho A \delta x C_p T)}{\partial t} = (qA)|_x - (qA)|_{x+\delta x} - hP\delta x(T - T_\infty)$$

Dividing by δx and taking the limit of $\delta x \rightarrow 0$, we obtain,

$$\frac{\partial(\rho A C_p T)}{\partial t} = -\frac{\partial(qA)}{\partial x} - hP(T - T_\infty)$$

Finally using the Fourier's law to replace q in terms of T ,

$$\boxed{\frac{\partial(\rho A C_p T)}{\partial t} = \frac{\partial}{\partial x} \left[kA \frac{\partial T}{\partial x} \right] - hP(T - T_\infty)} \quad (1.24)$$

Note that we have switched to partial derivatives as T is a function of both (x, t) and equation (1.24) is a partial differential equation. In addition to the boundary conditions specified in equation (1.23), we need

an initial condition at $t = 0$ to complete the problem specification. The conditions are

$$\begin{aligned} IC : T(x, t = 0) &= T_\infty, \\ BC1 : T(x = 0, t) &= T_0, \\ BC2 : T(x = L, t) &= T_\infty \end{aligned} \tag{1.25}$$