2.1.1 Uses of Mathematical Models

Without doubt, the most important result of developing a mathematical model of a chemical engineering system is the understanding that is gained of what really makes the process "tick." This insight enables you to strip away from the problem the many extraneous "confusion factors" and to get to the core of the system. You can see more clearly the cause-and-effect relationships between the variables.

Mathematical models can be useful in all phases of chemical engineering, from research and development to plant operations, and even in business and economic studies.

1. Research and development: determining chemical kinetic mechanisms and parameters from laboratory or pilot-plant reaction data; exploring the effects of different operating conditions for optimization and control studies; aiding in scale-up calculations.

2. Design: exploring the sizing and arrangement of processing equipment for dynamic performance; studying the interactions of various parts of the process, particularly when material recycle or heat integration is used; evaluating alternative process and control structures and strategies; simulating start-up, shutdown, and emergency situations and procedures.

3. Plant operation: troubleshooting control and processing problems; aiding in start-up and operator training; studying the effects of and the requirements for expansion (bottleneck-removal) projects; optimizing plant operation. It is usually much cheaper, safer, and faster to conduct the kinds of studies listed above on a mathematical model than experimentally on an operating unit. This is not to say that plant tests are not needed. As we will discuss later, they are a vital part of confirming the validity of the model and of verifying important ideas and recommendations that evolve from the model studies.

2.1.2 Scope of Coverage

We will discuss in this book only deterministic systems that can be described by ordinary or partial differential equations. Most of the emphasis will be on lumped systems (with one independent variable, time, described by ordinary differential equations). Both English and SI units will be used. You need to be familiar with both.

[Reference: William L Luyben - Process modeling, simulation, and control for chemical engineers-McGraw-Hill (1990)]

2.1.3 Principles of Formulation

A. BASIS. The bases for mathematical models are the fundamental physical and chemical laws, such as the laws of conservation of mass, energy, and momentum. To study dynamics we will use them in their general form with time derivatives included.

B. ASSUMPTIONS. Probably the most vital role that the engineer plays in modeling is in exercising his engineering judgment as to what assumptions can be validly made. Obviously an extremely rigorous model that includes every phenomenon down to microscopic detail would be so complex that it would take a long time to develop and might be impractical to solve, even on the latest super-computers. An engineering compromise between a rigorous description and getting an answer that is good enough is always required. This has been called "optimum sloppiness." It involves making as many simplifying assumptions as are reasonable without "throwing out the baby with the bath water." In practice, this optimum usually corresponds to a model which is as complex as the available computing facilities will permit. More and more this is a personal computer.

The development of a model that incorporates the basic phenomena occurring in the process requires a lot of skill, ingenuity, and practice. It is an area where the creativity and innovativeness of the engineer is a key element in the success of the process.

The assumptions that are made should be carefully considered and listed. They impose limitations on the model that should always be kept in mind when evaluating its predicted results.

C. MATHEMATICAL CONSISTENCY OF MODEL. Once all the equations of the mathematical model have been written, it is usually a good idea, particularly with big, complex systems of equations, to make sure that the number of variables equals the number of equations. The so-called "degrees of freedom" of the system must be zero in order to obtain a solution. If this is not true, the system is underspecified or overspecified and something is wrong with the formulation of the problem. This kind of consistency check may seem trivial, but I can testify from sad experience that it can save many hours of frustration, confusion, and wasted computer time.

Checking to see that the units of all terms in all equations are consistent is perhaps another trivial and obvious step, but one that is often forgotten. It is essential to be particularly careful of the time units of parameters in dynamic models. Any units can be used (seconds, minutes, hours, etc.), but they cannot be mixed. We will use "minutes" in most of our examples, but it should be remembered that many parameters are commonly on other time bases and need to be converted appropriately, e.g., overall heat transfer coefficients in $Btu/h\,°F\,ft^2$ or velocity in m/s. Dynamic simulation results are frequently in error because the engineer has forgotten a factor of "60" somewhere in the equations.

D. SOLUTION OF THE MODEL EQUATIONS. We will concern ourselves in detail with this aspect of the model in Part II. However, the available solution techniques and tools must be kept in mind as a mathematical model is developed. An equation without any way to solve it is not worth much.

E. VERIFICATION. An important but often neglected part of developing a mathematical model is proving that the model describes the real-world situation. At the design stage this sometimes cannot be done because the plant has not yet been built. However, even in this situation there are usually either similar existing plants or a pilot plant from which some experimental dynamic data can be obtained.

2.2 FUNDAMENTAL LAWS

In this section, some fundamental laws of physics and chemistry are reviewed in their general time-dependent form, and their application to some simple chemical systems is illustrated.

2.2.1 Continuity Equations

A. TOTAL CONTINUITY EQUATION (MASS BALANCE). The principle of the conservation of mass when applied to a dynamic system says

$$\begin{bmatrix} \text{Mass flow} \\ \text{into system} \end{bmatrix} - \begin{bmatrix} \text{mass flow} \\ \text{out of system} \end{bmatrix} = \begin{bmatrix} \text{time rate of change} \\ \text{of mass inside system} \end{bmatrix} \qquad (2.1)$$

The units of this equation are mass per time. Only one total continuity equation can be written for one system.

The normal steadystate design equation that we are accustomed to using says that "what goes in, comes out." The dynamic version of this says the same thing with the addition of the world "eventually."

The right-hand side of Eq. (2.1) will be either a partial derivative $\partial/\partial t$ or an ordinary derivative d/dt of the mass inside the system with respect to the independent variable t.

Example 2.1 Consider the tank of perfectly mixed liquid shown in Fig. 2.1 into which flows a liquid stream at a volumetric rate of F_0 (ft^3/min or m^3/min) and with a density of ρ_0 (lb$_m$/ft^3 or kg/m^3). The volumetric holdup of liquid in the tank is V (ft^3 or m^3), and its density is ρ. The volumetric flow rate from the tank is F, and the density of the outflowing stream is the same as that of the tank's contents.

The system for which we want to write a total continuity equation is all the liquid phase in the tank. We call this a macroscopic system, as opposed to a microscopic system, since it is of definite and finite size. The mass balance is around the whole tank, not just a small, differential element inside the tank.

$$F_0\,\rho_0 - F\rho = \text{time rate of change of } \rho V \qquad (2.2)$$

The units of this equation are lb$_m$/min or kg/min.

$$\left(\frac{ft^3}{min}\right)\left(\frac{lb_m}{ft^3}\right) - \left(\frac{ft^3}{min}\right)\left(\frac{lb_m}{ft^3}\right) = \frac{(ft^3)(lb_m/ft^3)}{min}$$

Since the liquid is perfectly mixed, the density is the same everywhere in the tank; it does not vary with radial or axial position; i.e., there are no spatial gradients in density in the tank. This is why we can use a macroscopic system. It also means that there is only one independent variable, t.

Since ρ and V are functions only of t, an ordinary derivative is used in Eq. (2.2).

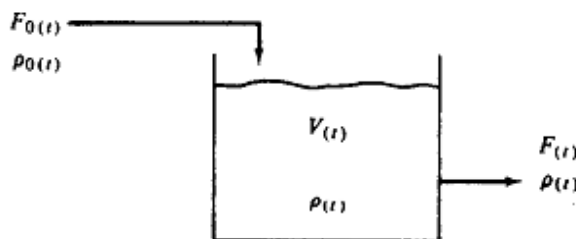$$\frac{d(\rho V)}{dt} = F_0\,\rho_0 - F\rho \qquad (2.3)$$

FIGURE 2.1
Perfectly mixed tank.

B. COMPONENT CONTINUITY EQUATIONS (COMPONENT BALANCES). Unlike mass, chemical components are not conserved. If a reaction occurs inside a system, the number of moles of an individual component will increase if it is a

product of the reaction or decrease if it is a reactant. Therefore the component continuity equation of thejth chemical species of the system says

$$\begin{bmatrix} \text{Flow of moles ofjth} \\ \text{component into system} \end{bmatrix} - \begin{bmatrix} \text{flow of moles ofjth} \\ \text{component out of system} \end{bmatrix}$$

$$+ \begin{bmatrix} \text{rate of formation of moles of jth} \\ \text{component from chemical reactions} \end{bmatrix}$$

$$= \begin{bmatrix} \text{time rate of change of moles of jth} \\ \text{component inside system} \end{bmatrix} \quad (2.9)$$

The units of this equation are moles of component j per unit time.

The flows in and out can be both convective (due to bulk flow) and molecular (due to diffusion). We can write one component continuity equation for each component in the system. If there are NC components, there are NC component continuity equations for any one system. However, the ~~one~~ total mass balance and these NC component balances are not all independent, since the sum of all the moles times their respective molecular weights equals the total mass. Therefore a given system has only NC independent continuity equations. We usually use the total mass balance and NC − 1 component balances. For example, in a binary (two-component) system, there would be one total mass balance and one component balance.

Example 2.3. Consider the same tank of perfectly mixed liquid that we used in Example 2.1 except that a chemical reaction takes place in the liquid in the tank. The system is now a CSTR (continuous stirred-tank reactor) as shown in Fig. 2.3. Component A reacts irreversibly and at a specific reaction rate k to form product, component B.

$$A \xrightarrow{k} B$$
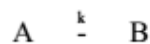
Let the concentration of component A in the inflowing feed stream be C_{A0} (moles of A per unit volume) and in the reactor C_A. Assuming a simple first-order reaction, the rate of consumption of reactant A per unit volume will be directly proportional to the instantaneous concentration of A in the tank. Filling in the terms in Eq. (2.9) for a component balance on reactant A,

$$\text{Flow of A into system} = F_0 C_{A0}$$

$$\text{Flow of A out of system} = F C_A$$

$$\text{Rate of formation of A from reaction} = - V k C_A$$

FIGURE 2.3
CSTR.
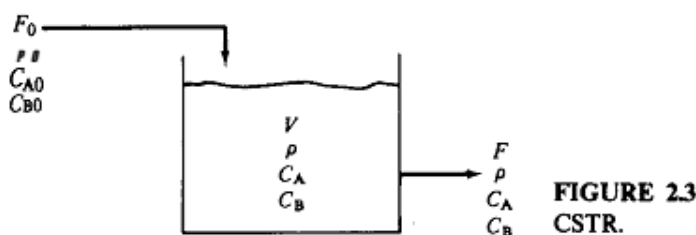
The minus sign comes from the fact that A is being consumed, not produced. The units of all these terms must be the same: moles of A per unit time. Therefore the VkC_A term must have these units, for example $(ft^3)(min^{-1})(moles$ of $A/ft^3)$. Thus the units of k in this system are min^{-1}.

$$\text{Time rate of change of A inside tank} = \frac{d(VC_A)}{dt}$$

Combining all of the above gives

$$\frac{d(VC_A)}{dt} = F_0 C_{A0} - FC_A - VkC_A \tag{2.10}$$

We have used an ordinary derivative since t is the only independent variable in this lumped system. The units of this component continuity equation are moles of A per unit time. The left-hand side of the equation is the dynamic term. The first two terms on the right-hand side are the convective terms. The last term is the generation term.

Since the system is binary (components A and B), we could write another component continuity equation for component B. Let C_B be the concentration of B in moles of B per unit volume.
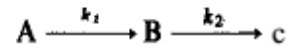
$$\frac{d(VC_B)}{dt} = F_0 C_{B0} - FC_B + VkC_A$$

Note the plus sign before the generation term since B is being produced by the reaction. Alternatively we could use the total continuity equation [Eq. (2.3)] since C_A, C_B, and ρ are uniquely related by

$$M_A C_A + M_B C_B = \rho \tag{2.11}$$

where M_A and M_B are the molecular weights of components A and B, respectively.

Example 2.4. Suppose we have the same macroscopic system as above except that now consecutive reactions occur. Reactant A goes to B at a specific reaction rate k_1, but B can react at a specific reaction rate k_2 to form a third component C.

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C$$

Assuming first-order reactions, the component continuity equations for components A, B, and C are

$$\frac{d(VC_A)}{dt} = F_0 C_{A0} - FC_A - Vk_1 C_A$$

$$\frac{d(VC_B)}{dt} = F_0 C_{B0} - FC_B + Vk_1 C_A - Vk_2 C_B \qquad (2.12)$$

$$\frac{d(VC_C)}{dt} = F_0 C_{C0} - FC_C + Vk_2 C_B$$

The component concentrations are related to the density

$$\sum_{j=A}^{C} M_j C_j = \rho \qquad (2.13)$$

Three component balances could be used or we could use two of the component balances and a total mass balance.

2.2.2 Energy Equation

The first law of thermodynamics puts forward the principle of conservation of energy. Written for a general "open" system (where flow of material in and out of the system can occur) it is

$$
\begin{bmatrix} \text{Flow of internal, kinetic, and} \\ \text{potential energy into system} \\ \text{by convection or diffusion} \end{bmatrix} - \begin{bmatrix} \text{flow of internal, kinetic, and} \\ \text{potential energy out of system} \\ \text{by convection or diffusion} \end{bmatrix}
$$

$$
+ \begin{bmatrix} \text{heat added to system by} \\ \text{conduction, radiation, and} \\ \text{reaction} \end{bmatrix} - \begin{bmatrix} \text{work done by system on} \\ \text{surroundings (shaft work and} \\ \text{PV work)} \end{bmatrix}
$$

$$
= \begin{bmatrix} \text{time rate of change of internal, kinetic,} \\ \text{and potential energy inside system} \end{bmatrix} \quad (2.18)
$$

Example 2.6. The CSTR system of Example 2.3 will be considered again, this time with a cooling coil inside the tank that can remove the exothermic heat of reaction λ (Btu/lb . mol of A reacted or **cal/g** · mol of A reacted). We use the normal convention that λ is negative for an exothermic reaction and positive for an endothermic reaction. The rate of heat generation (energy per time) due to reaction is the rate of consumption of A times λ.

$$
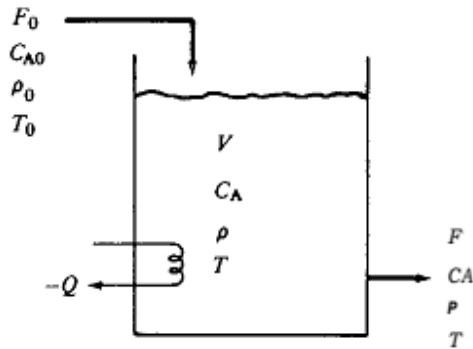Q_G = -\lambda V C_A k \quad (2.19)
$$

FIGURE 2.5
CSTR with heat removal.

The rate of heat removal from the reaction mass to the cooling coil is $-Q$ (energy per time). The temperature of the feed stream is T_0 and the temperature in the reactor is T (°R or K). Writing Eq. (2.18) for this system,

$$F_0 \rho_0 (U_0 + K_0 + \phi_0) - F\rho(U + K + \phi) + (Q_G + Q)$$

$$- (W + FP - F_0 P_0) = \frac{d}{dt}[(U + K + \phi)V\rho] \qquad (2.20)$$

where U = internal energy (energy per unit mass)
K = kinetic energy (energy per unit mass)
ϕ = potential energy (energy per unit mass)
W = shaft work done by system (energy per time)
P = pressure of system
P_0 = pressure of feed stream

Note that all the terms in Eq. (2.20) must have the same units (energy per time) so the FP terms must use the appropriate conversion factor (778 $ft \cdot lb_f/Btu$ in English engineering units).

In the system shown in Fig. 2.5 there is no shaft work, so $W = 0$. If the inlet and outlet flow velocities are not very high, the kinetic-energy term is negligible. If the elevations of the inlet and outlet flows are about the same, the potential-energy term is small. Thus Eq. (2.20) reduces to

$$\frac{d(\rho V U)}{dt} = F_0 \rho_0 U_0 - F\rho U + Q_G + Q - F\rho \frac{P}{\rho} + F_0 \rho_0 \frac{P_0}{\rho_0}$$

$$= F_0 \rho_0 (U_0 + P_0 \bar{V}_0) - F\rho(U + P\bar{V}) + Q_G + Q \qquad (2.21)$$

where $\bar{V}$ is the specific volume (ft^3/lb_m or m^3/kg), the reciprocal of the density. Enthalpy, H or h, is defined:

$$H \text{ or } h \equiv U + P\bar{V} \qquad (2.22)$$

We will use h for the enthalpy of a liquid stream and H for the enthalpy of a vapor stream. Thus, for the CSTR, Eq. (2.21) becomes

$$\frac{d(\rho V U)}{dt} = F_0 \rho_0 h_0 - F\rho h + Q - \lambda V k C_A \qquad (2.23)$$

For liquids the $P\bar{V}$ term is negligible compared to the U term, and we use the time rate of change of the enthalpy of the system instead of the internal energy of the system.

$$\frac{d(\rho V h)}{dt} = F_0 \rho_0 h_0 - F\rho h + Q - \lambda V k C_A \qquad (2.24)$$

The enthalpies are functions of composition, temperature, and pressure, but primarily temperature. From thermodynamics, the heat capacities at constant pressure, C_p, and at constant volume, C_v, are

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad (2.25)$$

To illustrate that the energy is primarily influenced by temperature, let us simplify the problem by assuming that the liquid enthalpy can be expressed as a product of absolute temperature and an average heat capacity C_p (Btu/lb$_m$°R or cal/g K) that is constant.

$$h = C_p T$$

We will also assume that the densities of all the liquid streams are constant. With these simplifications Eq. (2.24) becomes

$$\rho C_p \frac{d(VT)}{dt} = \rho C_p (F_0 T_0 - FT) + Q - \lambda V k C_A \qquad (2.26)$$

Example 2.7. To show what form the energy equation takes for a two-phase system, consider the CSTR process shown in Fig. 2.6. Both a liquid product stream F and a vapor product stream F_v (volumetric flow) are withdrawn from the vessel. The pressure in the reactor is P. Vapor and liquid volumes are V_v and V. The density and temperature of the vapor phase are ρ_v and T_v. The mole fraction of A in the vapor is y. If the phases are in thermal equilibrium, the vapor and liquid temperatures are equal ($T = T_v$). If the phases are in phase equilibrium, the liquid and vapor compositions are related by Raoult's law, a relative volatility relationship or some other vapor-liquid equilibrium relationship (see Sec. 2.2.6). The enthalpy of the vapor phase H (Btu/lb$_m$ or cal/g) is a function of composition y, temperature T_v, and pressure P. Neglecting kinetic-energy and potential-energy terms and the work term,
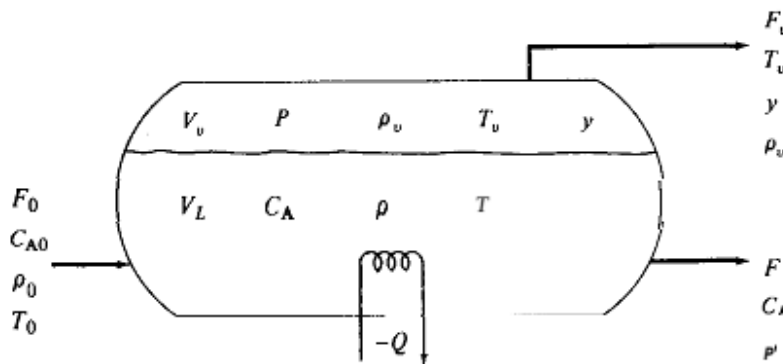

FIGURE 2.6
Two-phase CSTR with heat removal.

and replacing internal energies with enthalpies in the time derivative, the energy equation of the system (the vapor and liquid contents of the tank) becomes

$$\frac{d(\rho_v V_v H + \rho V_L h)}{dt} = F_0 \rho_0 h_0 - F \rho h - F_v \rho_v H + Q - \lambda V k C_A \qquad (2.27)$$

In order to express this equation explicitly in terms of temperature, let us again use a very simple form for h ($h = C_p T$) and an equally simple form for H.

$$H = C_p T + \lambda_v \qquad (2.28)$$

where λ_v is an average heat of vaporization of the mixture. In a more rigorous model λ_v could be a function of temperature T_v, composition y, and pressure P. Equation (2.27) becomes

$$\frac{d[\rho_v V_v (C_p T + \lambda_v) + \rho V_L C_p T]}{dt} = F_0 \rho_0 C_p T_0 - F \rho C_p T$$

$$- F_v \rho_v (C_p T + \lambda_v) + Q - \lambda V k C_A \qquad (2.29)$$

3.2 SERIES OF ISOTHERMAL, CONSTANT-HOLDUP CSTRs

The system is sketched in Fig. 3.1 and is a simple extension of the CSTR considered in Example 2.3. Product B is produced and reactant A is consumed in each of the three perfectly mixed reactors by a first-order reaction occurring in the liquid. For the moment let us assume that the temperatures and holdups (volumes) of the three tanks can be different, but both temperatures and the liquid volumes are assumed to be constant (isothermal and constant holdup). Density is assumed constant throughout the system, which is a binary mixture of A and B.

With these assumptions in mind, we are ready to formulate our model. If the volume and density of each tank are constant, the total mass in each tank is constant. Thus the total continuity equation for the first reactor is

$$\frac{d(\rho V_1)}{dt} = \rho F_0 - \rho F_1 = 0 \tag{3.1}$$

or $F_1 = F_0$.

Likewise total mass balances on tanks 2 and 3 give

$$F_3 = F_2 = F_1 = F_0 \equiv F \tag{3.2}$$

where F is defined as the throughput (m^3/min).

We want to keep track of the amounts of reactant A and product B in each tank, so component continuity equations are needed. However, since the system is binary and we know the total mass of material in each tank, only one component continuity equation is required. Either B or A can be used. If we arbitrarily choose A, the equations describing the dynamic changes in the amounts of
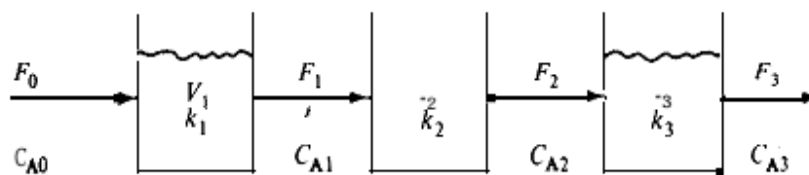

FIGURE 3.1
Series of CSTRs.

reactant A in each tank are (with units of kg · mol of **A/min**)

$$V_1 \frac{dC_{A1}}{dt} = F(C_{A0} - C_{A1}) - V_1 k_1 C_{A1}$$

$$V_2 \frac{dC_{A2}}{dt} = F(C_{A1} - C_{A2}) - V_2 k_2 C_{A2} \qquad (3.3)$$

$$V_3 \frac{dC_{A3}}{dt} = F(C_{A2} - C_{A3}) - V_3 k_3 C_{A3}$$

The specific reaction rates k_n are given by the Arrhenius equation

$$k_n = \alpha e^{-E/RT_n} \qquad n = 1, 2, 3 \qquad (3.4)$$

If the temperatures in the reactors are different, the k's are different. The n refers to the stage number.

The volumes V_n can be pulled out of the time derivatives because they are constant (see Sec. 3.3). The flows are all equal to F but can vary with time. An energy equation is not required because we have assumed isothermal operation. Any heat addition or heat removal required to keep the reactors at constant temperatures could be calculated from a steadystate energy balance (zero time derivatives of temperature).

The three first-order nonlinear ordinary differential equations given in Eqs. (3.3) are the mathematical model of the system. The parameters that must be known are $V_1, V_2, V_3, k_1, k_2,$ and k_3. The variables that must be specified before these equations can be solved are F and C_{A0}. "Specified" does *not* mean that they must be constant. They can be time-varying, but they must be known or given functions of time. They are the *forcing functions*.

The initial conditions of the three concentrations (their values at time equal zero) must also be known.

Let us now check the degrees of freedom of the system. There are three equations and, with the parameters and forcing functions specified, there are only three unknowns or dependent variables: $C_{A1}, C_{A2},$ and C_{A3}. Consequently a solution should be possible, as we will demonstrate in Chap. 5.

We will use this simple system in many subsequent parts of this book. When we use it for controller design and stability analysis, we will use an even simpler version. If the throughput F is constant and the holdups and temperatures are the same in all three tanks, Eqs. (3.3) become

$$\frac{dC_{A1}}{dt} + \left(k + \frac{1}{\tau}\right) C_{A1} = \frac{1}{\tau} C_{A0}$$

$$\frac{dC_{A2}}{dt} + \left(k + \frac{1}{\tau}\right) C_{A2} = \frac{1}{\tau} C_{A1} \qquad (3.5)$$

$$\frac{dC_{A3}}{dt} + \left(k + \frac{1}{\tau}\right) C_{A3} = \frac{1}{\tau} C_{A2}$$

where $\tau = V/F$ with units of minutes.

There is only one forcing function or input variable, C_{A0}.

3.3 CSTRs WITH VARIABLE HOLDUPS

If the previous example is modified slightly to permit the volumes in each reactor to vary with time, both total and component continuity equations are required for each reactor. To show the effects of higher-order kinetics, assume the reaction is now nth-order in reactant A.

Reactor 1:

$$\frac{dV_1}{dt} = F_0 - F_1$$

$$\frac{d}{dt}(V_1 C_{A1}) = F_0 C_{A0} - F_1 C_{A1} - V_1 k_1 (C_{A1}) \tag{3.6}$$

Reactor 2:

$$\frac{dV_2}{dt} = F_1 - F_2$$

$$\frac{d}{dt}(V_2 C_{A2}) = F_1 C_{A1} - F_2 C_{A2} - V_2 k_2 (C_{A2}) \tag{3.7}$$

Reactor 3 :

$$\frac{dV_3}{dt} = F_2 - F_3$$

$$\frac{d}{dt}(V_3 C_{A3}) = F_2 C_{A2} - F_3 C_{A3} - V_3 k_3 (C_{A3}) \tag{3.8}$$

Our mathematical model now contains six first-order nonlinear ordinary differential equations. Parameters that must be known are k_1, k_2, k_3, and n. Initial conditions for all the dependent variables that are to be integrated must be given: $C_{A1}, C_{A2}, C_{A3}, V_1, V_2,$ and V_3. The forcing functions $C_{A0(t)}$ and $F_{0(t)}$ must also be given.

Let us now check the degrees of freedom of this system. There are six equations. But there are nine unknowns: $C_{A1}, C_{A2}, C_{A3}, V_1, V_2, V_3, F_1, F_2,$ and F_3. Clearly this system is not sufficiently specified and a solution could not be obtained.

What have we missed in our modeling? A good plant operator could take one look at the system and see what the problem is. We have not specified how the flows out of the tanks are to be set. Physically there would probably be control valves in the outlet lines to regulate the flows. How are these control valves to be set? A common configuration is to have the level in the tank controlled by the outflow, i.e., a level controller opens the control valve on the exit

line to increase the outflow if the level in the tank increases. Thus there must be a relationship between tank holdup and flow.

$$F_1 = f_{(V_1)} \qquad F_2 = f_{(V_2)} \qquad F_3 = f_{(V_3)} \qquad (3.9)$$

The f functions will describe the level controller and the control valve. These three equations reduce the degrees of freedom to zero.

It might be worth noting that we could have considered the flow from the third tank F_3 as the forcing function. Then the level in tank 3 would probably be maintained by the flow into the tank, F_2. The level in tank 2 would be controlled by F_1, and tank 1 level by F_0. We would still have three equations.

The reactors shown in Fig. 3.1 would operate at atmospheric pressure if they were open to the atmosphere as sketched. If the reactors are not vented and if no inert blanketing is assumed, they would run at the bubblepoint pressure for the specified temperature and varying composition. Therefore the pressures could be different in each reactor, and they would vary with time, even though temperatures are assumed constant, as the C_A's change.

III. **TWO Heated Tanks :-** The flow rate F of oil passing through two Perfectly mixed tanks in series is constant with units m^3/min. The density ρ of the oil is const with units kg/m^3. The heat capacity C_p $(Kcal/kg\ K))$ is constant. The volume of the first tank V_1 is constant. And volume of the second tank V_2 is also const. but both are different. the temperature of the oil entering the first tank is T_0. The temperatures in the two tanks are T_1 & T_2. A heating coil in the first tank uses steam to heat the oil. Let Q be the heat addition rate in the first tank.
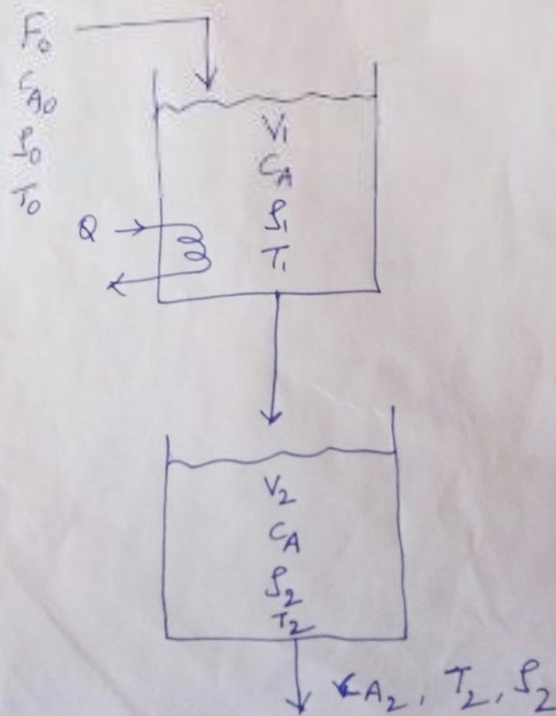
There is one energy balance for each tank, and each will be similar to Eq. (2.26) except there is no reaction involved in this process.

Energy balance for tank 1:

$$\frac{d(\rho C_p V_1 T_1)}{dt} = \rho C_p(F_0 T_0 - F_1 T_1) + Q_1 \qquad (3.10)$$

Energy balance for tank 2:

$$\frac{d(\rho C_p V_2 T_2)}{dt} = \rho C_p(F_1 T_1 - F_2 T_2) \qquad (3.11)$$

Since the throughput is constant $F_0 = F_1 = F_2 = F$. Since volumes, densities, and heat capacities are all constant, Eqs. (3.10) and (3.11) can be simplified.

$$\rho C_p V_1 \frac{dT_1}{dt} = \rho C_p F(T_0 - T_1) + Q_1 \qquad (3.12)$$

$$\rho C_p V_2 \frac{dT_2}{dt} = \rho C_p F(T_1 - T_2) \qquad (3.13)$$

Let's check the degrees of freedom of this system. The parameter values that are known are ρ, C_p, V_1, V_2, and F. The heat input to the first tank Q_1 would be set by the position of the control valve in the steam line. In later chapters we will use this example and have a temperature controller send a signal to the steam valve to position it. Thus we are left with two dependent variables, T_1 and T_2, and we have two equations. So the system is correctly specified.

3.5 GAS-PHASE, PRESSURIZED CSTR

Suppose a mixture of gases is fed into the reactor sketched in Fig. 3.2. The reactor is filled with reacting gases which are perfectly mixed. A reversible reaction occurs :

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$
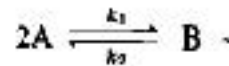
The forward reaction is 1.5th-order in A; the reverse reaction is first-order in B. Note that the stoichiometric coefficient for A and the order of the reaction are not the same. The mole fraction of reactant A in the reactor is y. The pressure inside the vessel is P (absolute). Both P and y can vary with time. The volume of the reactor V is constant.

We will assume an isothermal system, so the temperature T is constant. Perfect gases are also assumed. The feed stream has a density ρ_0 and a mole fraction y_0 of reactant A. Its volumetric flow rate is F_0.

The flow out of the reactor passes through a restriction (control valve) into another vessel which is held at a constant pressure P_D (absolute). The outflow will vary with the pressure and the composition of the reactor. Flows through control valves are discussed in more detail in Part III; here let us use the formula

$$F = C_v \sqrt{\frac{P - P_D}{\rho}} \qquad (3.14)$$

C_v is the valve-sizing coefficient. Density varies with pressure and composition.

$$\rho = \frac{MP}{RT} = [yM_A - (1 - y)M_B] \frac{P}{RT} \qquad (3.15)$$

where M = average molecular weight
  M_A = molecular weight of reactant A
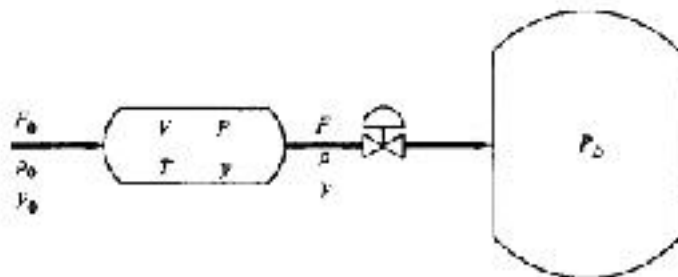 M_B = molecular weight of product B

FIGURE 3.2
Gas-phase CSTR

The concentration of reactant in the reactor is

$$C_A = \frac{Py}{RT} \tag{3.16}$$

with units of moles of A per unit volume. The overall reaction rate for the forward reaction is

$$\mathcal{R}_F = k_1(C_A)^{1.5} = -\frac{1}{2V}\left(\frac{dn_A}{dt}\right)_R = \frac{1}{V}\left(\frac{dn_B}{dt}\right)_R$$

The overall reaction rate for the reverse reaction is

$$\mathcal{R}_R = k_2 C_B = \frac{1}{2V}\left(\frac{dn_A}{dt}\right)_R = -\frac{1}{V}\left(\frac{dn_B}{dt}\right)_R$$

With these fundamental relationships pinned down, we are ready to write the total and component continuity equations.

Total continuity :

$$V\frac{d\rho}{dt} = \rho_0 F_0 - \rho F \tag{3.17}$$

Component A continuity:

$$V\frac{dC_A}{dt} = F_0 C_{A0} - FC_A - 2Vk_1(C_A)^{1.5} + 2Vk_2 C_B \tag{3.18}$$

The 2 in the reaction terms comes from the stoichiometric coefficient of A.

There are five equations [Eqs. (3.14) through (3.18)] that make up the mathematical model of this system. The parameters that must be known are V, C_v, k_1, k_2, R, M_A, and M_B. The forcing functions (or inputs) could be P_D, ρ_0, F_0, and C_{A0}. This leaves five unknowns (dependent variables): C_A, ρ, P, F, and y.

IV. NONISOTHERMAL CSTR :-

1) An irreversible, exothermic reaction is carried out in a single, perfectly mixed CSTR as shown in figure

$$A \xrightarrow{K} B$$

The reaction is n^{th} order in reactant 'A' and has a heat of reaction λ (kcal/kgmol of 'A' reacted).

Assumptions :-

1) negligible heat losses and constant densities are assumed.

To remove the heat of reaction, a cooling jacket surrounds the reactor. Cooling water is added to the Jacket at a volumetric flow rate F_J and with an inlet temperature of T_{J0}. The volume of water in the Jacket is constant. The heat loss due to (mass of the) metal wall is assumed negligible. this assumption is often a fairly good assumption but the heat capacity of steel is only about 0.1 Btu/(lbm°F), which is an order of magnitude less than that of water.

(a)

(A) Perfectly mixed cooling Jacket:

③ we assume that the temperature everywhere in the Jacket is T_J. the heat transfer btn the process at temperature 'T' and the cooling water at temperature T_J is described by an overall H.T. coefficient.

$$Q = UA_H (T - T_J)$$

where,

Q = Heat transfer rate

U = Overall H.T. Coefficient.

A_H = H.T. area.

Note:- In general the heat transfer area could vary with the holdup in the reactor if some area was not completely connected with reaction mass liquid at all times.

Reactor total continuity:-

$$\int \frac{dV}{dt} = \int_0 F_0 - \int F$$

$$\frac{dV}{dt} = F_0 - F \quad\quad\quad ①$$

Reactor component 'A' continuity:-

$$F_0 C_{A0} - F C_A - V K C_A = \frac{d(VC_A)}{dt} \quad\quad ②$$

Reactor Energy Equations:-

②

$\mathcal{E}_0 F_0 \mathcal{E}_0$

$\begin{bmatrix} \text{Flow of Internal, kinetic} \\ \text{and potential energy into} \\ \text{sys by convection or diffusion} \end{bmatrix} - \begin{bmatrix} \text{Flow of Internal, kinetic} \\ \text{& Potential energy out of} \\ \text{system by convection or} \\ \text{diffusion} \end{bmatrix}$

$+ \begin{bmatrix} \text{heat added to sys by} \\ \text{conduction, radiation &} \\ \text{reaction} \end{bmatrix} - \begin{bmatrix} \text{work done by sys} \\ \text{on surroundings} \\ (\text{shaft work & pv work}) \end{bmatrix}$

$= \begin{bmatrix} \text{Time rate of change of internal,} \\ \text{kinetic & potential energy inside system} \end{bmatrix}$

$$F_0 \rho_0 (U_0 + K_0 + \phi_0) - F\rho [U + K + \phi] + (Q_G + Q)$$

$$- (W + FP - F_0 P_0) = \frac{d[(U+K+\phi)V\rho]}{dt}$$

③

Whereas

$U = $ Internal Energy (energy per unit mass)

$K = $ Kinetic energy (energy per unit mass)

$\phi = $ potential energy (energy per unit mass)

$W = $ shaft work done by sys (energy per unit time)

$P = $ Pressure of the system

$P_0 = $ Pressure of the feed stream

 [Reference: William L Luyben - Process modeling, simulation, and control for chemical engineers-McGraw-Hill (1990)]

(20)

④ Assume that there is no shaft work, so, $W = 0$

⑤ Kinetic energy term is negligible, ~~due to~~ If the inlet & outlet flow velocities are not very high,

⑥ If the elevations of the Inlet & outlet flows are about the same (or) negligible difference, then potential energy term is small.

$$F_0 \rho_0 U_0 - F \rho U + Q_G + Q - F \rho \frac{P}{\rho} + F_0 \rho_0 \frac{P_0}{\rho_0}$$
$$= \frac{d(\rho V U)}{dt} \quad \text{—} \quad ④$$

$$F_0 \rho_0 (U_0 + P_0 \bar{V}_0) - F \rho (U + P \bar{V}) + Q_G + Q$$
$$= \frac{d(V \rho U)}{dt} \quad \text{—} \quad ⑤$$

Where,

$\bar{V} = $ specific volume (m^3/kg)

h (or) $H = U + P\bar{V}$

We will use h for enthalpy of a (liquid) stream, and H for the enthalpy of a vapor stream.

thus, for the CSTR Eqn ⑤ becomes

$$F_0 \rho_0 h_0 - F \rho h + Q - \lambda V k C_A = \frac{d(\rho V U)}{dt} \quad \text{—} \quad ⑥$$

$$\textcircled{E} \quad \int \frac{d(Vh)}{dt} = \int \left(F_0 h_0 - Fh \right) - \lambda V K(C_A)^2 - UA_H(T-T_J)$$

For liquids the $p\bar{v}$ term is negligible compared to the U' & we use the time rate of change of enthalpy of the system instead of internal energy of the system.

Jacket energy equation:-

$$F_J \int_J \left(h_{J_0} - h_J \right) + UA_H(T-T_J) = V_J \int_J \frac{dh_J}{dt}$$

where, $\int_J$ = density of cooling water

h = enthalpy of process liquid

h_J = enthalpy of cooling water

the enthalpies are functions of composition, temperature and pressure, but primarily temperature let us simplify the problem by assuming that the liquid enthalpy can be expressed as a product of absolute temperature and an average heat capacity C_p (kcal/kg k) that is const.

$$h = C_p T$$

$$h_J = C_J T_J$$

Heat capacity of process liq.

heat capacity of

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

const. densities

A hydraulic relation b/w reactor holdup and the the flow out of the reactor is also needed. A level controller is assumed to change the outflow as the volume in the tank rises (or) falls. the higher the volume, the larger the outflow. the outflow is shut off completely when the volume drops to a minimum value V_{min}.

$$F = K_V (V - V_{min})$$

$\downarrow$

Proportionality const. for level controller.

$\downarrow$

P-only feed back controller.

$$\frac{dV}{dt} = F_0 - F \quad \text{——} \quad \text{①}$$

$$\frac{d(VC_A)}{dt} = F_0 C_{A_0} - FC_A - V(C_A)^2 \alpha e^{-E/RT} \quad \text{②}$$

$$\rho C_p \frac{d(VT)}{dt} = \rho C_p (F_0 T_0 - FT) - \lambda V(C_A)^n \alpha e^{-E/RT} - UA_H (T - T_J) \quad \text{③}$$

$$\rho_J V_J C_J \frac{dT_J}{dt} = F_J \rho_J C_J (T_{J0} - T_J) + UA_H (T - T_J) \quad \text{④}$$

$$F = K_V (V - V_{min}) \quad \text{——} \quad \text{⑤}$$

④

check the degrees of the freedom:-

Five, independent equations and five unknowns:

$$V, F, C_A, T, \& T_J$$

Forcing functions are $T_0, F_0, C_{A0} \& F_J$

The parameters that must be known are: $n, \alpha, E, R, \delta, C_p, U, A_H, \delta_J, \delta,$ C_J, T_{J0}, k_v and V_{min}

If A_H → varies with holdup of reactor

If the reactor flat bottomed vertical cylinder with dia D and if the jacket is only around the outside not around the bottom $\boxed{A_H = \dfrac{4}{D} V}$

 [Reference: William L Luyben - Process modeling, simulation, and control for chemical engineers-McGraw-Hill (1990)]

3.6 NONISOTHERMAL CSTR

In the reactors studied so far, we have shown the effects of variable holdups, variable densities, and higher-order kinetics on the total and component continuity equations. Energy equations were not needed because we assumed isothermal operations. Let us now consider a system in which temperature can change with time. An irreversible, exothermic reaction is carried out in a single perfectly mixed CSTR as shown in Fig. 3.3.

$$A \xrightarrow{k} B$$

The reaction is nth-order in reactant A and has a heat of reaction λ (Btu/lb · mol of A reacted). Negligible heat losses and constant densities are assumed.

To remove the heat of reaction, a cooling jacket surrounds the reactor. Cooling water is added to the jacket at a volumetric flow rate F_J and with an
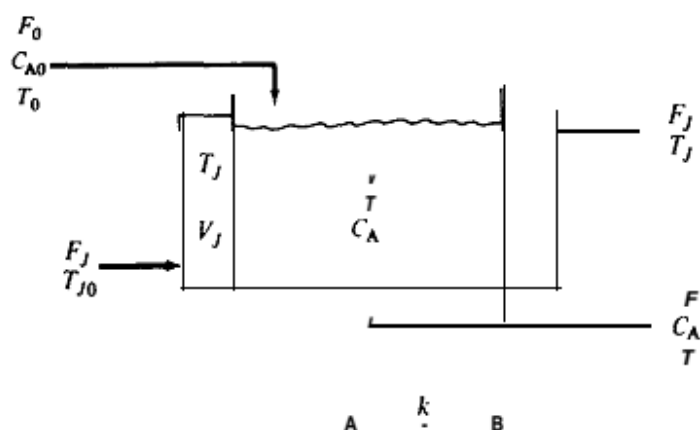

FIGURE 3.3
Nonisothermal CSTR.

inlet temperature of T_{J0}. The volume of water in the jacket V_J is constant. The mass of the metal walls is assumed negligible so the "thermal inertia" of the metal need not be considered. This is often a fairly good assumption because the heat capacity of steel is only about 0.1 Btu/lb$_m$°F, which is an order of magnitude less than that of water.

A. PERFECTLY MIXED COOLING JACKET. We assume that the temperature everywhere in the jacket is T_J. The heat transfer between the process at temperature T and the cooling water at temperature T_J is described by an overall heat transfer coefficient.

$$Q = UA_H(T - T_J) \qquad\qquad (3.19)$$

where Q = heat transfer rate
$\quad U$ = overall heat transfer coefficient
$\quad A_H$ = heat transfer area

In general the heat transfer area could vary with the holdup in the reactor if some area was not completely-d with reaction mass liquid at all times. The equations describing the system are:

Reactor total continuity:

$$\frac{dV}{dt} = F_0 - F$$

Reactor component A continuity :

$$\frac{d(VC_A)}{dt} = F_0\,C_{A0} - FC_A - Vk(C_A)$$

Reactor energy equation :

$$\rho\,\frac{d(Vh)}{dt} = \rho(F_0 h_0 - Fh) - \lambda Vk(C_A)^n - UA_H(T - T_J) \qquad (3.20)$$

Jacket energy equation :

$$\rho_J V_J\,\frac{dh_J}{dt} = F_J \rho_J(h_{J0} - h_J) + UA_H(T - T_J) \qquad (3.21)$$

where ρ_J = density of cooling water
$\quad h$ = enthalpy of process liquid
$\quad h_J$ = enthalpy of cooling water

The assumption of constant densities makes $C_p = C_v$ and permits us to use enthalpies in the time derivatives to replace internal energies,
$\quad$ A hydraulic- between reactor holdup and the flow out of the reactor is also needed. A level controller is assumed to change the outflow as the volume in the tank rises or falls: the higher the volume, the larger the outflow. The outflow is shut off completely when the volume drops to a minimum value V_{min} .

$$F = K_V(V - V_{min}) \qquad (3.22)$$

The level controller is a proportional-only feedback controller.

Finally, we need enthalpy data to relate the h's to compositions and temperatures. Let us assume the simple forms

$$h = C_p T \quad \text{and} \quad h_J = C_J T_J \tag{3.23}$$

where C_p = heat capacity of the process liquid
C_J = heat capacity of the cooling water

Using Eqs. (3.23) and the Arrhenius relationship for k, the five equations that describe the process are

$$\frac{dV}{dt} = F_0 - F \tag{3.24}$$

$$\frac{d(VC_A)}{dt} = F_0 C_{A0} - FC_A - V(C_A)^n \alpha e^{-E/RT} \tag{3.25}$$

$$\rho C_p \frac{d(VT)}{dt} = \rho C_p(F_0 T_0 - FT) - \lambda V(C_A)^n \alpha e^{-E/RT} - UA_H(T - T_J) \tag{3.26}$$

$$\rho_J V_J C_J \frac{dT_J}{dt} = F_J \rho_J C_J(T_{J0} - T_J) + UA_H(T - T_J) \tag{3.27}$$

$$F = K_V(V - V_{min}) \tag{3.28}$$

Checking the degrees of freedom, we see that there are five equations and five unknowns: $V, F, C_A, T,$ and T_J. We must have initial conditions for these five dependent variables. The forcing functions are $T_0, F_0, C_{A0},$ and F_J.

The parameters that must be known are $n, a, E, R, p, C,, U, A,, \rho_J, V,,$ $C_J, T_{J0}, K_V,$ and V_{min}. If the heat transfer area varies with the reactor holdup it would be included as another variable, but we would also have another equation; the relationship between area and holdup. If the reactor is a flat-bottomed vertical cylinder with diameter D and if the jacket is only around the outside, not around the bottom

$$A_H = \frac{4}{D} V \tag{3.29}$$

We have assumed the overall heat transfer coefficient U is constant. It may be a function of the coolant flow rate F_J or the composition of the reaction mass, giving one more variable but also one more equation.

3.7 SINGLE-COMPONENT VAPORIZER

Boiling systems represent some of the most interesting and important operations in chemical engineering processing and are among the most **difficult** to model. To describe these systems rigorously, conservation equations must be written for both the vapor and liquid phases. The basic problem is finding the rate of vaporization of material from the liquid phase into the vapor phase. The equations used to describe the boiling rate should be physically reasonable and mathematically convenient for solution.

Consider the vaporizer sketched in Fig. 3.6. Liquefied petroleum gas (LPG) is fed into a pressurized tank to hold the liquid level in the tank. We will assume that LPG is a pure component: propane. Vaporization of mixtures of components is discussed in Sec. 3.8.

The liquid in the tank is assumed perfectly mixed. Heat is added at a rate Q to hold the desired pressure in the tank by vaporizing the liquid at a rate W_v (mass per time). Heat losses and the mass of the tank walls are assumed negligible. Gas is drawn off the top of the tank at a volumetric flow rate F_v. F_v is the forcing function or load disturbance.

A. STEADYSTATE MODEL. The simplest model would neglect the dynamics of both vapor and liquid phases and relate the gas rate F_v to the heat input by

$$\rho_v F_v (H_v - h_0) = Q \qquad (3.34)$$

where H_v = enthalpy of vapor leaving tank (Btu/lb$_m$ or cal/g)
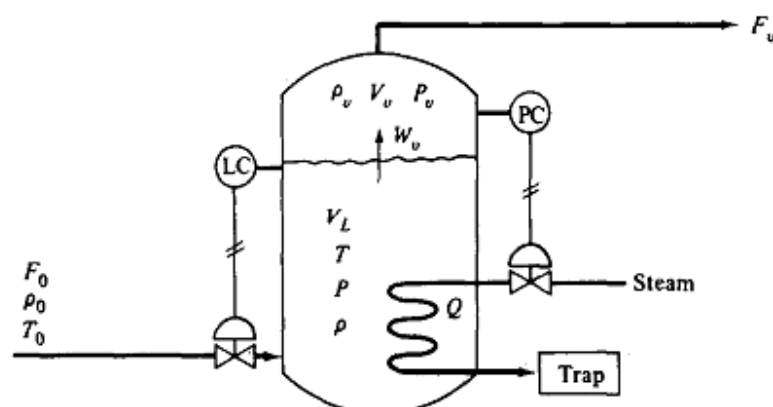h_0 = enthalpy of liquid feed (Btu/lb$_m$ or cal/g)

FIGURE 3.6
LPG vaporizer.

B. LIQUID-PHASE DYNAMICS MODEL. A somewhat more realistic model is obtained if we assume that the volume of the vapor phase is small enough to make its dynamics negligible. If only a few moles of liquid have to be vaporized to change the pressure in the vapor phase, we can assume that this pressure is always equal to the vapor pressure of the liquid at any temperature ($P = P_v$ and $W_v = \rho_v F_v$). An energy equation for the liquid phase gives the temperature (as a function of time), and the vapor-pressure relationship gives the pressure in the vaporizer at that temperature.

A total continuity equation for the liquid phase is also needed, plus the two controller equations relating pressure to heat input and liquid level to feed flow rate F_0. These feedback controller relationships will be expressed here simply as functions. In later parts of this book we will discuss these functions in detail.

$$Q = f_{1(P)} \qquad F_0 = f_{2(V_L)} \qquad (3.35)$$

An equation of state for the vapor is needed to be able to calculate density ρ_v from the pressure or temperature. Knowing any one property (T, P, or ρ_v) pins down all the other properties since there is only one component, and two phases are present in the tank. The perfect-gas law is used.

The liquid is assumed incompressible so that $C_v = C_p$ and its internal energy is $C_p T$. The enthalpy of the vapor leaving the vaporizer is assumed to be of the simple form: $C_p T + I_v$.

Total continuity :

$$\rho \frac{dV_L}{dt} = \rho_0 F_0 - \rho_v F_v \qquad (3.36)$$

Energy :

$$C_p \rho \frac{d(V_L T)}{dt} = \rho_0 C_p F_0 T_0 - \rho_v F_v (C_p T + \lambda_v) + Q \qquad (3.37)$$

State :

$$\rho_v = \frac{MP}{RT} \qquad (3.38)$$

Vapor pressure :

$$\ln P = \frac{A}{T} + B \qquad (3.39)$$

Equations (3.35) to (3.39) give us six equations. Unknowns are Q, F_0, P, V_L, ρ_v, and T.

3.8 MULTICOMPONENT FLASH DRUM

Let us look now at vapor-liquid systems with more than one component. A liquid stream at high temperature and pressure is "flashed" into a drum, i.e., its pressure is reduced as it flows through a restriction (valve) at the inlet of the drum. This sudden expansion is irreversible and occurs at constant enthalpy. If it were a reversible expansion, entropy (not enthalpy) would be conserved. If the drum pressure is lower than the bubblepoint pressure of the feed at the feed temperature, some of the liquid feed will vaporize.

    Gas is drawn off the top of the drum through a control valve whose stem position is set by a pressure controller (Fig. 3.7). Liquid comes off the bottom of the tank on level control.

    The pressure P_0 before the pressure letdown valve is high enough to prevent any vaporization of feed at its temperature T_0 and composition x_{0j} (mole fraction jth component). The forcing functions in this system are the feed temperature T_0, feed rate F, and feed composition x_{0j}. Adiabatic conditions (no heat losses) are assumed. The density of the liquid in the tank, ρ_L, is assumed to be a known function of temperature and composition.
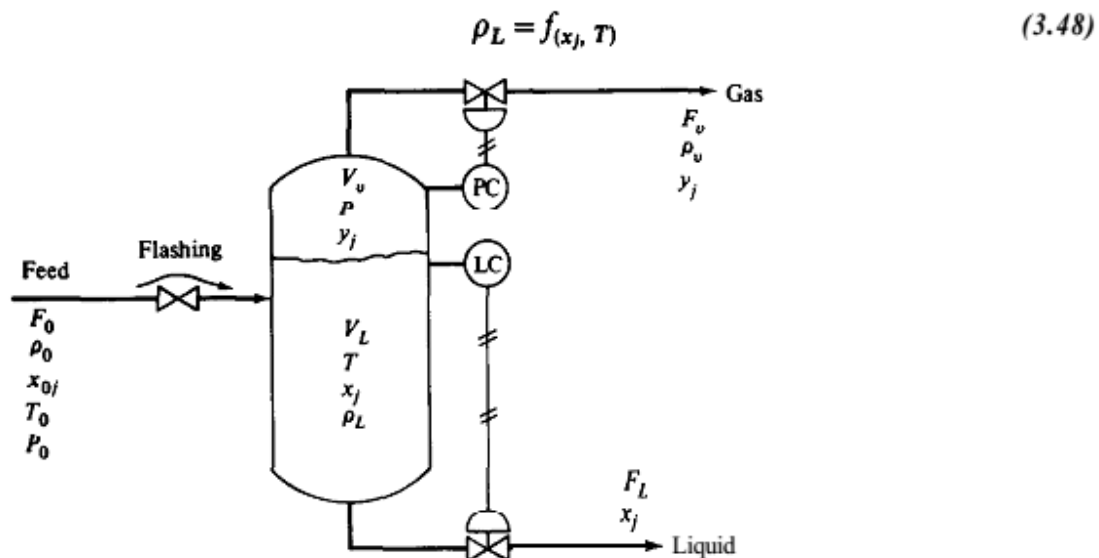
$$\rho_L = f_{(x_j, T)} \qquad (3.48)$$

FIGURE 3.7
Flash drum.

The density ρ_t of the vapor in the drum is a known function of temperature T, composition y_j and pressure P. If the perfect-gas law can be used,

$$\rho_t = \frac{M_v^{av} P}{R T} \qquad (3.49)$$

where M_t^{av} is the average molecular weight of the gas.

$$M_v^{av} = \sum_{j=1}^{NC} M_j y_j \qquad (3.50)$$

where M_j is the molecular weight of the jth component.

A. STEADYSTATE MODEL. The simplest model of this system is one that neglects dynamics completely. Pressure is assumed constant, and the steadystate total and component continuity equations and a steadystate energy balance are used. Vapor and liquid phases are assumed to be in equilibrium.

Total continuity:

$$\rho_0 F_0 = \rho_v F_t + \rho_L F_L \qquad (3.51)$$

Component continuity:

$$\frac{\rho_0 F_0}{M_0^{av}} x_{0j} \frac{\rho_v}{M_v^{av}} F_t y_j + \frac{\rho_L F_L}{M_L^{av}} x_j \qquad (3.52)$$

Vapor-liquid equilibrium :

$$y_j = f_{(x_j, T, P)} \qquad (3.53)$$

Energy equation :

$$h_0 \rho_0 F_0 = H \rho_v F_t + h \rho_L F_L \qquad (3.54)$$

Thermal properties :

$$h_0 = f_{(x_{0j},\, T_0)} \qquad h = f_{(x_j,\, T)} \qquad H = f_{(y_j,\, T,\, P)} \qquad (3.55)$$

The average molecular weights M^{av} are calculated from the mole fractions in the appropriate stream [see Eq. (3.50)]. The number of variables in the system is $9 + 2(NC - 1)$: ρ_v, F_v, M_v^{av}, y_1, y_2, ... y_{NC-1}, ρ_L, F_L, M_L^{av}, x_1, x_2, . .., x_{NC-1}, T, h, and H. Pressure P and all the feed properties are given. There are NC — 1 component balances [Eq. (3.52)].

There are a total of NC equilibrium equations. We can say that there are NC equations like Eq. (3.53). This may bother some of you. Since the sum of the y's has to add up to 1, you may feel that there are only NC — 1 equations for the y's. But even if you think about it this way, there is still one more equation: The sum of the partial pressures has to add up to the total pressure. Thus, whatever way you want to look at it, there are NC phase equilibrium equations.

	Equation	Number of equations
Total continuity	(3.5 1)	1
Energy	(3.54)	1
Component continuity	(3.52)	"NC-1
Vapor-liquid equilibrium	(3.53)	NC
Densities of vapor and liquid	(3.48) and (3.49)	2
Thermal properties for liquid and vapor streams	(3.55)	2
Average molecular weights	(3.50)	2
		$\overline{2NC + 7}$

The system is specified by the algebraic equations listed above. This is just a traditional steadystate "equilibrium-flash" calculation.

3.11 IDEAL BINARY DISTILLATION COLUMN

Next to the ubiquitous CSTR, the distillation column is probably the most popular and important process studied in the chemical engineering literature. Distillation is used in many chemical processes for separating feed streams and for purification of final and intermediate product streams.

Most columns handle multicomponent feeds. But many can be approximated by binary or pseudobinary mixtures. For this example, however, we will make several additional assumptions and idealizations that are sometimes valid but more frequently are only crude approximations.

The purpose of studying this simplified case first is to reduce the problem to its most elementary form so that the basic structure of the equations can be clearly seen. In the next example, a more realistic system will be modeled.

We will assume a binary system (two components) with constant relative volatility throughout the column and theoretical (100 percent efficient) trays, i.e., the vapor leaving the tray is in equilibrium with the liquid on the tray. This means the simple vapor-liquid equilibrium relationship can be used

$$y_n = \frac{\alpha x_n}{1 + (a - 1)x_n} \qquad (3.77)$$

where x_n = liquid composition on the nth tray (mole fraction more volatile component)

y_n = vapor composition on the nth tray (mole fraction more volatile component)

α = relative volatility

A single feed stream is fed as saturated liquid (at its bubblepoint) onto the feed tray N,. See Fig. 3.12. Feed flow rate is F (mol/min) and composition is z (mole fraction more volatile component). The overhead vapor is totally condensed in a condenser and flows into the reflux drum, whose holdup of liquid is M_D (moles). The contents of the drum is assumed to be perfectly mixed with composition x_D. The liquid in the drum is at its bubblepoint. Reflux is pumped back to the top tray (N_T) of the column at a rate R. Overhead distillate product is removed at a rate D.

We will neglect any delay time (deadtime) in the vapor line from the top of the column to the reflux drum and in the reflux line back to the top tray (in industrial-scale columns this is usually a good assumption, but not in small-scale laboratory columns). Notice that y_{NT} is not equal, dynamically, to x_D. The two are equal only at steadystate.

At the base of the column, liquid bottoms product is removed at a rate B and with a composition x_B. Vapor **boilup** is generated in a thermosiphon reboiler at a rate V. Liquid circulates from the bottom of the column through the tubes in the vertical tube-in-shell reboiler because of the smaller density of the vapor-liquid mixture in the reboiler tubes. We will assume that the liquids in the reboiler and in the base of the column are perfectly mixed together and have the same composition x_B and total holdup M_B (moles). The circulation rates through well-designed thermosiphon reboilers are quite high, so this assumption is usually a good one. The composition of the vapor leaving the base of the column and entering tray 1 is y_B. It is in equilibrium with the liquid with composition x_B.

The column contains a total of N_T theoretical trays. The liquid holdup on each tray including the downcomer is M_n. The liquid on each tray is assumed to be perfectly mixed with composition x,. The holdup of the vapor is assumed to be negligible throughout the system. Although the vapor volume is large, the number of moles is usually small because the vapor density is so much smaller than the liquid density. This assumption breaks down, of course, in high-pressure columns.

A further assumption we will make is that of equimolal overflow. If the molar heats of vaporization of the two components are about the same, whenever one mole of vapor condenses, it vaporizes a mole of liquid. Heat losses up the column and temperature changes from tray to tray (sensible-heat effects) are assumed negligible. These assumptions mean that the vapor and liquid rates through the stripping and rectifying sections will be constant under steadystate conditions. The "operating lines" on the familiar McCabe-Thiele diagram are straight lines.

However, we are interested here in dynamic conditions. The assumptions above, including negligible vapor holdup, mean that the vapor rate through all
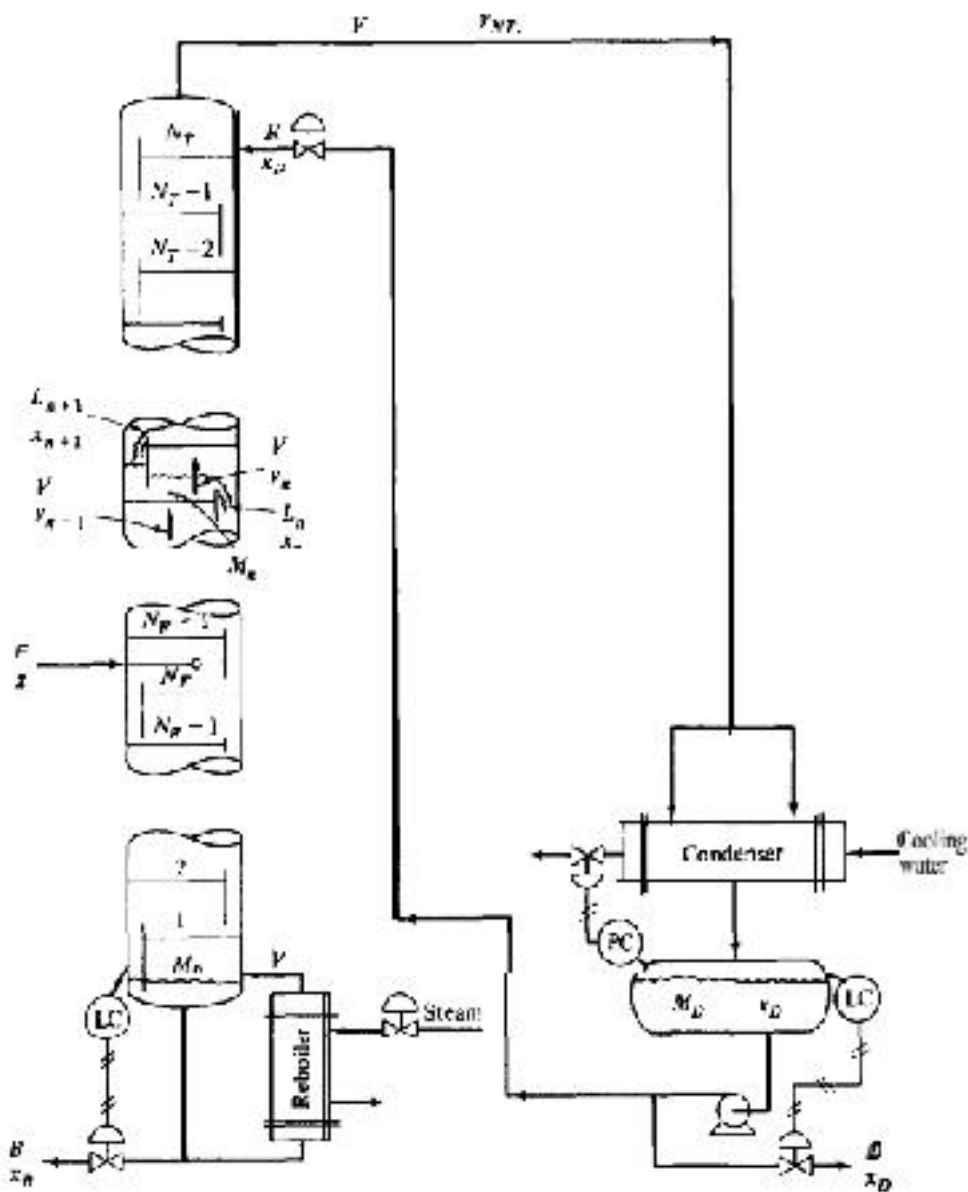

FIGURE 3.12
Binary distillation column.

trays of the column is the same, dynamically as well as at steadystate.

$$V = V_1 = V_2 = V_3 = \cdots = V_{NT}$$

Remember these V's are not necessarily constant with time. The vapor **boilup** can be manipulated dynamically. The mathematical effect of assuming equimolal **overflow** is that we do not need an energy equation for each tray. This- is quite a significant simplification.

The liquid rates throughout the' column will not be the same dynamically. They will depend on the fluid mechanics of the tray. Often a simple Francis weir formula relationship is used to relate the liquid holdup on the tray $(M,)$ to the liquid flow rate leaving the tray (L_n).

$$F_L = 3.33 L_w (h_{ow})^{1.5} \tag{3.78}$$

where F_L = liquid flow rate over weir (ft^3/s)
$\quad L_w$ = length of weir (ft)
$\quad h_{ow}$ = height of liquid over weir (ft)

More rigorous relationships can be obtained from the detailed tray hydraulic equations to include the effects of vapor rate, densities, compositions, etc. We will assume a simple functional relationship between liquid holdup and liquid rate.

$$M_n = f_{(L_n)} \tag{3.79}$$

Finally, we will neglect the dynamics of the condenser and the reboiler. In commercial-scale columns, the dynamic response of these heat exchangers is usually ·much faster than the response of the column itself. In some systems, however, the dynamics of this peripheral equipment are important and must be included in the model.

With all these assumptions in mind, we are ready to write the equations describing the system. Adopting the usual convention, our total continuity equations are written in terms of moles per unit time. This is kosher because no chemical reaction is assumed to occur in the column.

Condenser and **Reflux** *Drum*

Total continuity:

$$\frac{dM_D}{dt} = V - R - D \tag{3.80}$$

Component continuity (more volatile component):

$$\frac{d(M_D x_D)}{dt} = V y_{NT} - (R + D) x_D \tag{3.81}$$

Top Tray (n = N_T*)*

Total continuity:

$$\frac{dM_{NT}}{dt} = R - L_{NT} \tag{3.82}$$

for chemical engineers-McGraw-Hill (1990)]

Component continuity :

$$\frac{d(M_{NT}x_{NT})}{dt} = Rx_D - L_{NT}\,x_{NT} + V y_{NT-1} - V y_{NT} \tag{3.83}$$

Next to Top Tray $(n = N_T - 1)$

Total continuity:

$$\frac{dM_{NT-1}}{dt} = L_{NT} - L_{NT-1} \tag{3.84}$$

Component continuity :

$$\frac{d(M_{NT-1}\,x_{NT-1})}{dt} = L_{NT}x_{NT} - L_{NT-1}x_{NT-1} + V y_{NT-2} - V y_{NT-1} \tag{3.85}$$

nth Tray

Total continuity:

$$\frac{dM_n}{dt} = L_{n+1} - L_n \tag{3.86}$$

Component continuity:

$$\frac{d(M_n x_n)}{dt} = L_{n+1} x_{n+1} - L_n x_n + V y_{n-1} - V y_n \tag{3.87}$$

Feed Tray $(n = N_F)$

Total continuity:

$$\frac{dM_{NF}}{dt} = L_{NF+1} - L_{NF} + F \tag{3.88}$$

Component continuity :

$$\frac{d(M_{NF}\,x_{NF})}{dt} = L_{NF+1}\,x_{NF+1} - L_{NF}\,x_{NF} + V y_{NF-1} - V y_{NF} + Fz \tag{3.89}$$

First Tray $(n = 1)$

Total continuity :

$$\frac{dM_1}{dt} = L_2 - L_1 \tag{3.90}$$

Component continuity :

$$\frac{d(M_1 x_1)}{dt} = L_2 x_2 - L_1 x_1 + V y_B - V y_1 \tag{3.91}$$

Reboiler and Column Base

Total continuity:

$$\frac{dM_B}{dt} = L_1 - V - B \tag{3.92}$$

Component continuity :

$$\frac{d(M_B x_B)}{dt} = L_1 x_1 - V y_B - Bx, \tag{3.93}$$

Each tray and the column base have equilibrium equations [Eq. (3.77)]. Each tray also has a hydraulic equation [Eq. (3.79)]. We also need two equations representing the level controllers on the column base and reflux drum shown in Fig. 3.12.

$$D = f_{1(M_D)} \qquad B = f_{2(M_B)} \tag{3.94}$$

Let us now examine the degrees of freedom of the system. The feed rate F and composition z are assumed to be given.

Number of variables :

Tray compositions (x_n and y_n)	$= 2N_T$
Tray liquid flows (L_n)	$= N_T$
Tray liquid holdups (M,)	$= N_T$
Reflux drum composition (x_D)	$= 1$
Reflux drum flows (R and D)	$= 2$
Reflux drum holdup (M,)	$= 1$
Base compositions (x_B and y_B)	$= 2$
Base flows (V and B)	$= 2$
Base holdup (M_B)	$= 1$
	$\overline{4N_T + 9}$

Number of equations :

		Equation number
Tray component continuity	$= N_T$	(3.87)
Tray total continuity	$= N_T$	(3.86)
Equilibrium (trays plus base)	$= N_T + 1$	(3.77)
Hydraulic	$= N_T$	(3.79)
Level controllers	$= 2$	(3.94)
Reflux drum component continuity	$= 1$	(3.8 1)
Reflux drum total continuity	$= 1$	(3.80)
Base component continuity	$= 1$	(3.93)
Base total continuity	$= 1$	(3.92)
	$\overline{4N_T + 7}$	

Therefore the system is underspecified by two equations. From a control engineering viewpoint this means that there are only *two* variables that can be

controlled (can be fixed). The two variables that must somehow be specified are reflux flow R and vapor **boilup** V (or heat input to the reboiler). They can be held constant (an **openloop** system) or they can be changed by two controllers to try to hold some other two variables constant. In a digital simulation of this column in Part II we will assume that two feedback controllers adjust R and V to control overhead and bottoms compositions x_D and x_B .

$$R = f_{1(x_D)} \qquad V = f_{2(x_B)} \qquad (3.95)$$