

# Numerical Analysis Module 1

## Abstract Equation Forms in Process Modeling

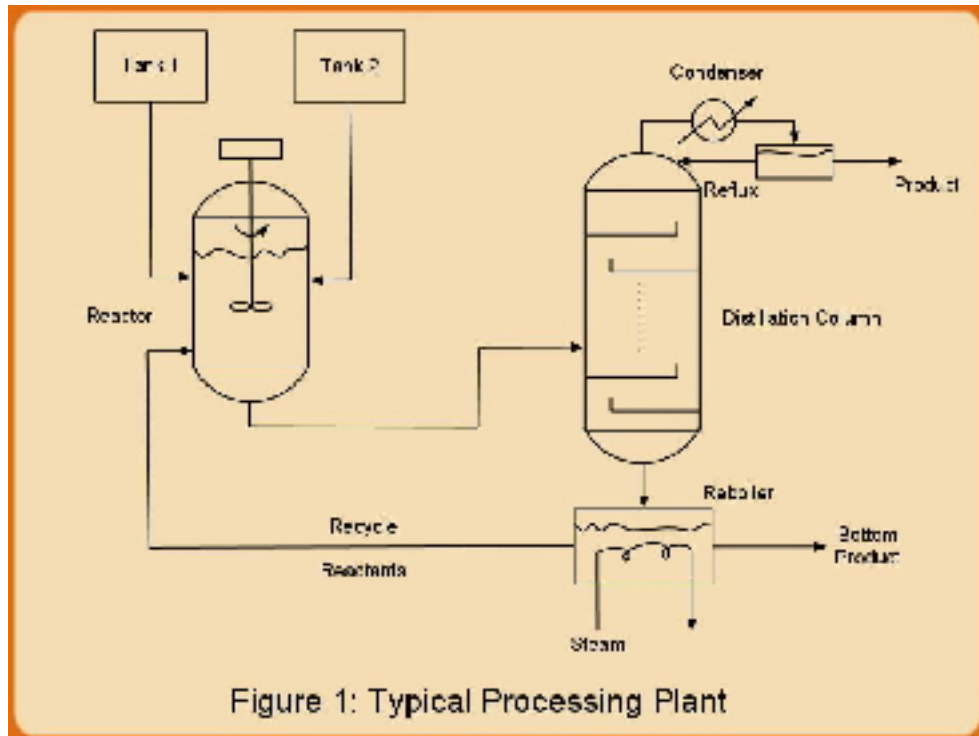
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## Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Mechanistic Models and Equation Forms</b>	<b>5</b>
2.1	Linear Algebraic Equations . . . . .	5
2.2	<b>Nonlinear Algebraic Equations</b> . . . . .	6
2.3	Optimization Based Formulations . . . . .	9
2.4	Ordinary Differential Equations - Initial Value Problem (ODE-IVP) . . . . .	11
<b>3</b>	<b>Differential Algebraic Equations</b>	<b>21</b>
3.1	Partial Differential Equations (PDEs) and ODE-Boundary value Problems (ODE-BVP) . . . . .	23
<b>4</b>	<b>Summary</b>	<b>28</b>

## 1 Introduction

A modern chemical plant consists of interconnected units such as heat exchangers, reactors, distillation columns, mixers etc. with high degree of integration to achieve energy efficiency. Design and operation of such complex plants is a challenging problem. Mathematical modeling and simulation is a cost effective method of designing or understanding



behavior of these chemical plants when compared to study through experiments. Mathematical modeling cannot substitute experimentation, however, it can be effectively used to plan the experiments or creating scenarios under different operating conditions. Thus, best approach to solving most chemical engineering problems involves judicious combination of mathematical modeling and carefully planned experiments.

To begin with, let us look at types of problems that can arise in context of modeling and simulation. Consider a typical small chemical plant consisting of a reactor and a distillation column, which is used to separate the product as overhead (see Figure 1). The reactants, which are separated as bottom product of the distillation column, are recycled to the reactor. We can identify following problems

- **Process Design problem**

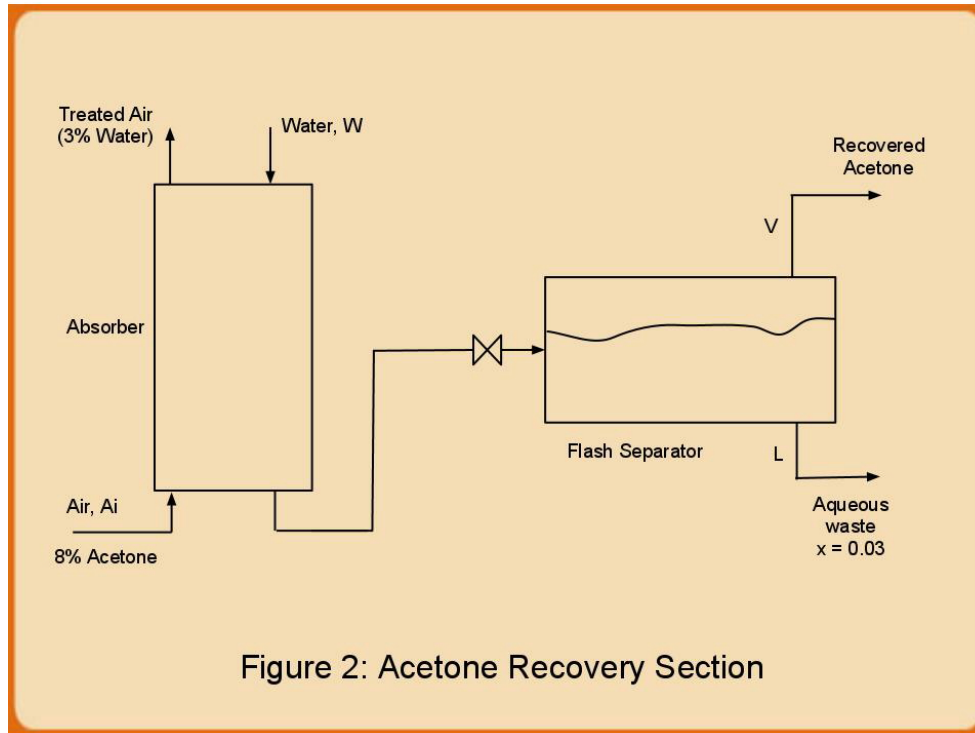
*Given:* Desired product composition, raw material composition and availability.

- *To Find:* Raw material flow rates, reactor volume and operating conditions (temperature, pressure etc.), distillation column configuration (feed locations and product draws), reboiler, condenser sizes and operating conditions (recycle and reflux flows, steam flow rate, operating temperatures and pressure etc.)

- **Process Retrofitting:** Improvements in the existing set-up or operating conditions  
Plant may have been designed for certain production capacity and assuming certain raw material quality. We are often required to assess whether
  - Is it possible to operate the plant at a different production rate?
  - What is the effect of changes in raw material quality?
  - Is it possible to make alternate arrangement of flows to reduce energy consumption?
- **Dynamic behavior and operability analysis:** Any plant is designed by assuming certain ideal composition of raw material quality, temperature and operating temperatures and pressures of utilities. In practice, however, it is impossible to maintain all the operating conditions exactly at the nominal design conditions. Changes in atmospheric conditions of fluctuations in steam header pressure, cooling water temperature, feed quality fluctuations, fouling of catalysts, scaling of heat transfer surfaces etc. keep perturbing the plant from the ideal operating condition. Thus, it becomes necessary to understand transient behavior of the system in order to
  - reject of effects of disturbances on the key operating variables such as product quality
  - achieve transition from one operating point to an economically profitable operating point.
  - carry out safety and hazard analysis

In order to solve process design or retrofitting problems, mathematical models are developed for each unit operation starting from first principles. Such mechanistic (or first principles) models in Chemical Engineering are combination of mass, energy and momentum balances together with associated rate equations, equilibrium relation and equations of state.

- **Mass balances:** overall, component.
- **Rate equations:** mass, heat and momentum transfer rates (constitutive equations.), rate of chemical reactions
- **Equilibrium principles :** physical (between phases) and chemical (reaction rate equilibrium).



- **Equations of state:** primarily for problems involving gases.

From mathematical viewpoint, these models can be classified into two broad classes

- *Distributed parameter model:* These models capture the relationship between the variables involved as functions of time and space.
- *Lumped parameter models:* These models lump all spatial variation and all the variables involved are treated as functions time alone.

The above two classes of models together with the various scenarios under consideration give rise to different types of equation forms such as linear / nonlinear algebraic equations, ordinary differential equations or partial differential equations. In order to provide motivation for studying these different kinds of equation forms, we present examples of different models in chemical engineering and derive abstract equation forms in the following section.

## 2 Mechanistic Models and Equation Forms

### 2.1 Linear Algebraic Equations

Plant wide or section wide mass balances are carried out at design stage or later during operation for keeping material audit. These models are typical examples of systems of simultaneous linear algebraic equations..

**Example 1** *Recovery of acetone from air -acetone mixture is achieved using an absorber and a flash separator (Figure 2). A model for this system is developed under following conditions*

- *All acetone is absorbed in water*
- *Air entering the absorber contains no water vapor*
- *Air leaving the absorber contains 3 mass % water vapor*

*The flash separator acts as a single equilibrium stage such that acetone mass fraction in vapor and liquid leaving the flash separator is related by relation*

$$y = 20.5x \quad (1)$$

*where  $y$  mass fraction of the acetone in the vapor stream and  $x$  mass fraction of the acetone in the liquid stream. Operating conditions of the process are as follows*

- *Air in flow: 600 lb/hr with 8 mass % acetone*
- *Water flow rate: 500 lb/hr*

*It is required that the waste water should have acetone content of 3 mass % and we are required to determine concentration of the acetone in the vapor stream and flow rates of the product streams.*

*Mass Balance:*

$$0.92A_i = 0.97A_o \quad (\text{Air}) \quad (2)$$

$$0.08 A_i = 0.03 L + y V \quad (\text{Acetone}) \quad (3)$$

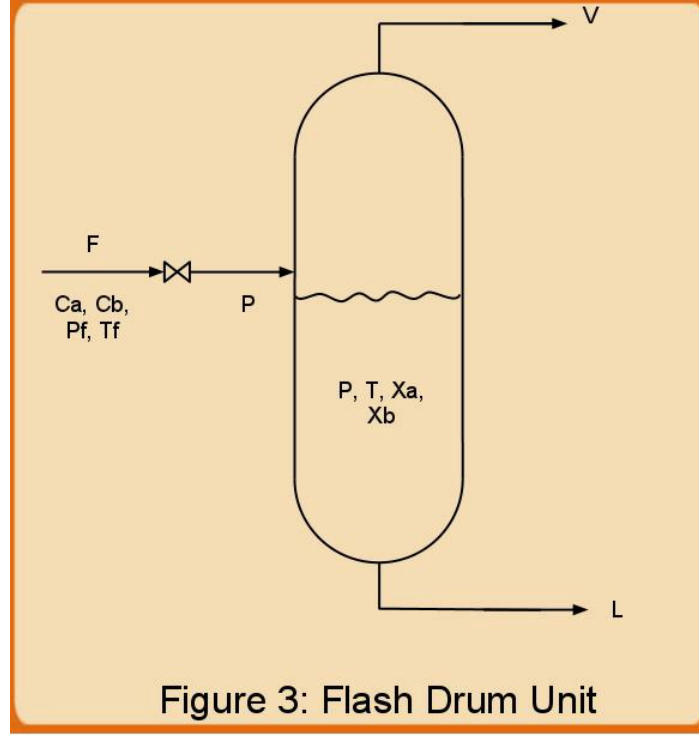
$$W = 0.03 A_o + (1 - y)V + 0.97L \quad (\text{Water}) \quad (4)$$

$$x = 0.03 \quad (\text{Design requirement}) \quad (5)$$

*Equilibrium Relation:*

$$y = 20.5x \quad (6)$$

$$\Rightarrow y = 20.5 \times 0.03 = 0.615 \quad (7)$$



*Substituting for all the known values and rearranging, we have*

$$\begin{bmatrix} 0.97 & 0 & 0 \\ 0 & 0.03 & 0.615 \\ 0.03 & 0.385 & 0.97 \end{bmatrix} \begin{bmatrix} Ao \\ L \\ V \end{bmatrix} = \begin{bmatrix} 0.92 \times 600 \\ 0.08 \times 600 \\ 500 \end{bmatrix} \quad (8)$$

The above model is a typical example of system of linear algebraic equations, which have to be solved simultaneously. The above equation can be represented in abstract form set of linear algebraic equations

$$A\mathbf{x} = \mathbf{b} \quad (9)$$

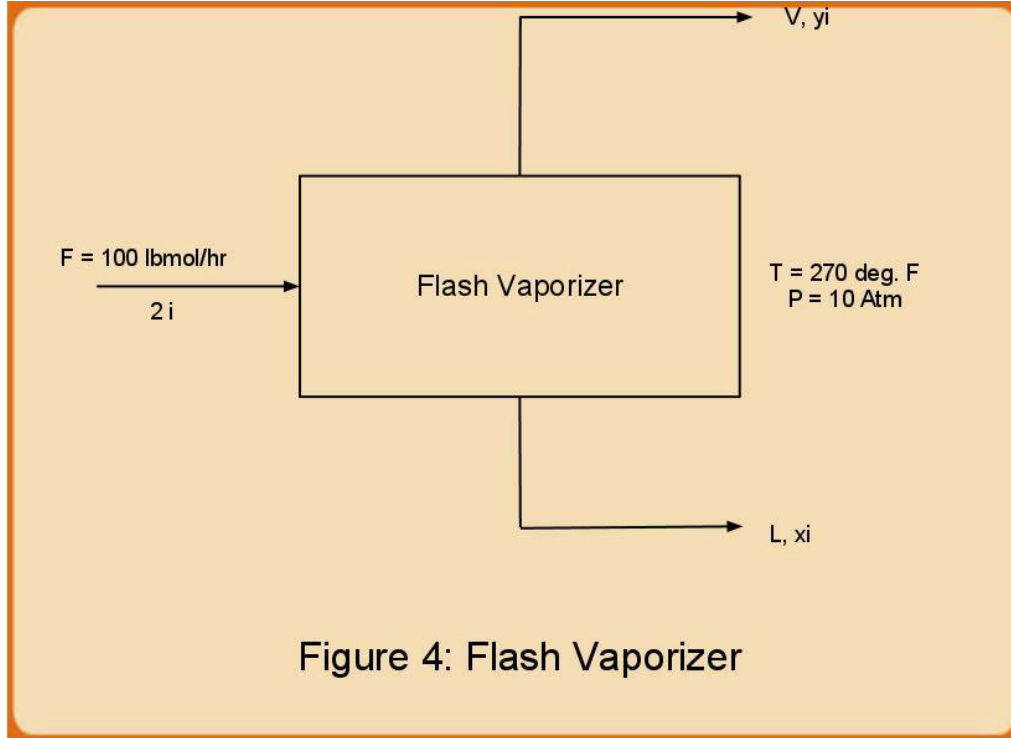
where  $\mathbf{x}$  and  $\mathbf{b}$  are a  $(n \times 1)$  vectors (i.e.  $\mathbf{x}, \mathbf{b} \in R^n$ ) and  $A$  is a  $(n \times n)$  matrix.

## 2.2 Nonlinear Algebraic Equations

Consider a stream of two components A and B at a high pressure  $P_f$  and temperature  $T_f$  as shown in Figure 3. If the  $P_f$  is greater than the bubble point pressure at  $T_f$ , no vapor will be present. The liquid stream passes through a restriction (valve) and is flashed in the drum, i.e. pressure is reduced from  $P_f$  to  $P$ . This abrupt expansion takes place under constant enthalpy. If the pressure  $P$  in the flash drum is less than the bubble point pressure

Table 1: Flash vaporization Unit Example: k-values and compositions

Component	$z_i$	$k_i$
n-butane	0.25	2.13
n-pentane	0.45	1.10
n-hexane	0.30	0.59



of the liquid feed at  $T_f$ , the liquid will partially vaporize and two phases at the equilibrium with each other will be present in the flash drum. The equilibrium relationships are

- Temperature of the liquid phase = temperature of the vapor phase.
- Pressure of the liquid phase = pressure of the vapor phase.
- Chemical potential of the  $i$ 'th component in the liquid phase = Chemical potential of the  $i$ 'th component in the vapor phase

**Example 2** Consider flash vaporization unit shown in Figure 4. A hydrocarbon mixture containing 25 mole % of n butane, 45 mole % of n-hexane is to be separated in a simple flash vaporization process operated at 10 atm. and 270°F. The equilibrium  $k$ - values at this composition are reported in Table 1. Let  $x_i$  represent mole fraction of the component  $i$

in liquid phase and  $y_i$  represent mole fraction of the component  $i$  in vapor phase. Model equations for the flash vaporizer are

- Equilibrium relationships

$$k_i = y_i/x_i \quad (i = 1, 2, 3) \quad (10)$$

- Overall mass balance

$$F = L + V \quad (11)$$

- Component balance

$$z_i F = x_i L + y_i V \quad (i = 1, 2, 3) \quad (12)$$

$$= x_i L + k_i x_i V \quad (13)$$

$$\sum x_i = 1 \quad (14)$$

Note that this results in a set of simultaneous 5 nonlinear algebraic equations in 5 unknowns Equations (11-14) can be written in abstract form as follows

$$f_1(x_1, x_2, x_3, L, V) = 0 \quad (15)$$

$$f_2(x_1, x_2, x_3, L, V) = 0 \quad (16)$$

$$\dots\dots\dots = 0$$

$$f_5(x_1, x_2, x_3, L, V) = 0 \quad (17)$$

which represent coupled nonlinear algebraic equations. These equations have to be solved simultaneously to find solution vector

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & x_3 & L & V \end{bmatrix}^T \quad (18)$$

The above 5 equations can also be further simplified as follows

$$x_i = z_i / \left[ 1 + \left( \frac{V}{F} \right) (k_i - 1) \right]$$

Using  $\sum x_i = 1$ , we have

$$f(V/F) = \sum \frac{z_i}{1 + (V/F)(k_i - 1)} - 1 = 0 \quad (19)$$

In general, we encounter  $n$  nonlinear algebraic equations in  $n$  variables, which have to be solved simultaneously. These can be expressed in the following abstract form

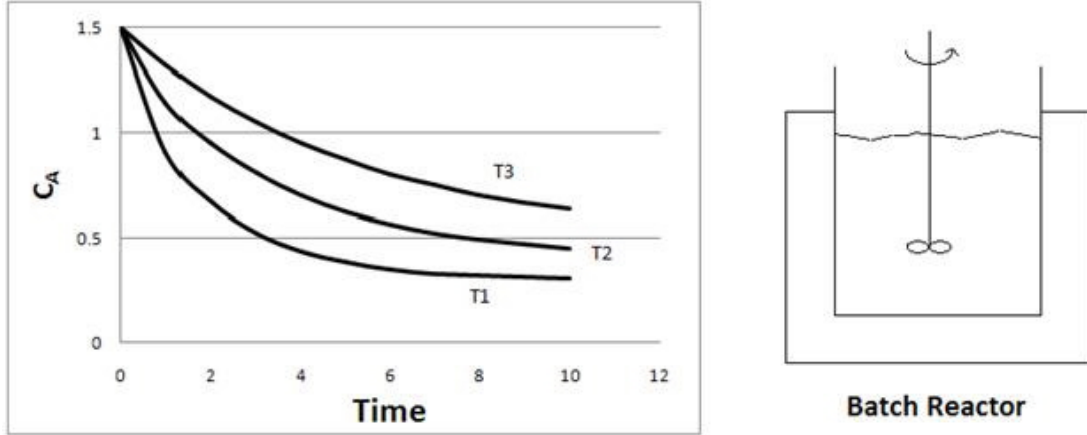
$$f_1(x_1, x_2, x_3, \dots, x_n) = 0 \quad (20)$$

$$f_2(x_1, x_2, x_3, \dots, x_n) = 0$$

$$\dots\dots\dots = 0 \quad (21)$$

$$f_n(x_1, x_2, x_3, \dots, x_n) = 0 \quad (22)$$





**Figure 5: Batch Reactor**

Using vector notation, we can write

$$\begin{aligned} F(\mathbf{x}) &= \bar{0} \quad ; \quad \mathbf{x} \in R^n \\ \mathbf{x} &= \begin{bmatrix} x_1 & x_2 & \dots & x_n \end{bmatrix}^T \end{aligned} \quad (23)$$

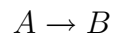
where  $\bar{0}$  represents  $n \times 1$  zero vector. Here  $F(\mathbf{x}) \in R^n$  represents  $n$  dimensional function vector defined as

$$F(\mathbf{x}) = \begin{bmatrix} f_1(\mathbf{x}) & f_2(\mathbf{x}) & \dots & f_n(\mathbf{x}) \end{bmatrix}^T \quad (24)$$

## 2.3 Optimization Based Formulations

Variety of modeling and design problems in chemical engineering are formulated as optimization problems.

**Example 3** Consider a simple reaction



modelled using the following reaction rate equation

$$-r_a = -dC_a/dt = k_o(C_a)^n \exp\left(\frac{-E}{RT}\right) \quad (25)$$

Table 2: Reaction Rates at Different Temperatures and Concentrations in a batch experiment

Reaction Rate	Concentration	Temperature
$-r_{a1}$	$C_{a1}$	$T_1$
$-r_{a2}$	$C_{a2}$	$T_2$
....	....	....
$-r_{aN}$	$C_{aN}$	$T_N$

carried out in a batch reactor (see Figure 5). It is desired to find the kinetic parameters  $k_o, E$  and  $n$  from the experimental data. The data reported in Table 5 is collected from batch experiments in a reactor at different temperatures

Substituting these values in the rate equation will give rise to  $N$  equations in three unknowns, which forms an overdetermined set equations. Due to experimental errors in the measurements of temperature and reaction rate, it may not be possible to find a set of values of  $\{k_o, E, n\}$  such that the reaction rate equation is satisfied at all the data points. However one can decide to select  $\{V_o, E, n\}$  such that the quantity

$$\Phi = \sum_{i=1}^N \left[ -r_{ai} - k_o (C_{ai})^n \exp\left(\frac{-E}{RT_i}\right) \right]^2 \quad (26)$$

is minimized with respect to  $\{k_o, E, n\}$ . Suppose we use  $-\hat{r}_{ai}$  to denote the estimated reaction rate

$$-\hat{r}_{ai} = k_o C_{ai}^n \exp\left(\frac{-E}{R * T_i}\right) \quad (27)$$

then, the problem is to choose parameters  $\{k_o, E, n\}$  such that the sum of the square of errors between the measured and estimated rates is minimum, i.e.

$$\underset{k_o, E, n}{Min} \quad \Phi(k_o, E, n) = \sum_{i=1}^N [-r_{ai} - (-\hat{r}_{ai})]^2 \quad (28)$$

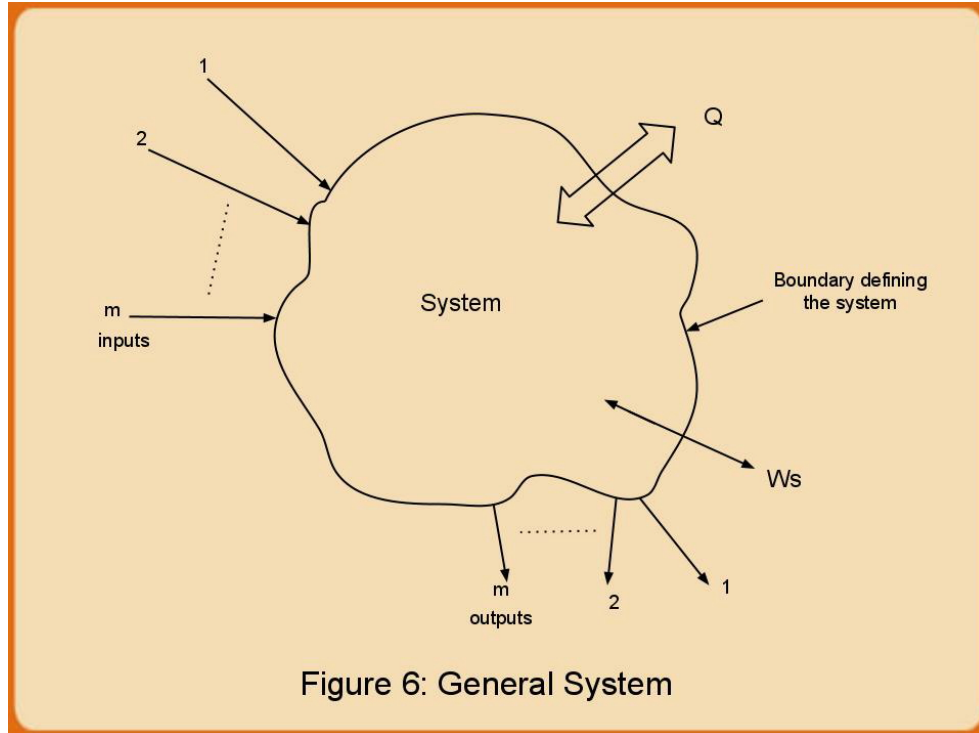
**Example 4** Cooling water is to be allocated to three distillation columns. Up to 8 million liters per day are available, and any amount up to this limit may be used. The costs of supplying water to each equipment are

$$\begin{aligned} \text{Equip. 1: } f_1 &= |1 - D_1| - 1 \quad \text{for } 0 \leq D_1 \leq 2 \\ &= 0 \quad (\text{otherwise}) \end{aligned}$$

$$\text{Equip. 2: } f_2 = -\exp\left(\frac{-1}{2}(D_2 - 5)^2\right) \quad \text{for } 0 \leq D_2 \leq \infty$$

$$\text{Equip. 3: } f_3 = D_3^2 - 6D_3 + 8 \quad \text{for } 0 \leq D_3 \leq 4$$

Minimize  $\Phi = \sum f_i$  to find  $D_1, D_2$ , and  $D_3$



*Note that this is an example of a typical multi-dimensional optimization problem, which can be expressed in abstract form*

$$\begin{array}{ll} \text{Min} & \Phi(\mathbf{x}) \\ \mathbf{x} & \end{array} \quad (29)$$

*where  $\mathbf{x} \in R^n$  and  $f(\mathbf{x}) : R^n \rightarrow R$  is a scalar objective function. A general problem of this type may include constraints on  $\mathbf{x}$  or functions of  $\mathbf{x}$ .*

## 2.4 Ordinary Differential Equations - Initial Value Problem (ODE-IVP)

For most of the processing systems of interest to the chemical engineer, there are three fundamental quantities :mass, energy and momentum. These quantities can be characterized by variables such as density, concentration, temperature, pressure and flow rate. These characterizing variables are called as state of the processing system. The equations that relate the state variables (dependent variables) to the independent variables are derived from application of conservation principle on the fundamental quantities and are called the state equations.

Let quantity S denote any one of the fundamental quantities

- Total mass
- Mass of the individual components
- Total energy.
- Momentum

Then, the principles of the conservation of the quantity S states that:

$$\frac{\text{Accumulation of S within a system}}{\text{Time Period}} = \frac{\text{Flow of S in the system}}{\text{Time Period}} - \frac{\text{Flow of S out of the system}}{\text{Time Period}} + \frac{\text{Amount of S generated within the system}}{\text{Time Period}} - \frac{\text{Amount of S consumed within the system}}{\text{Time Period}}$$

Figure 6 shows schematic diagram of a general system and its interaction with external world. Typical dynamic model equations are as follows:

#### **Total Mass Balance**

$$\frac{d(\rho V)}{dt} = \sum_{i:\text{inlet}} \rho_i F_i - \sum_{j:\text{outlet}} \rho_j F_j$$

#### **Mass Balance of the component A**

$$\frac{dn_a}{dt} = \frac{d(C_a V)}{dt} = \sum C_{ai} F_i - \sum C_{aj} F_j - rV \quad (30)$$

#### **Total energy Balance**

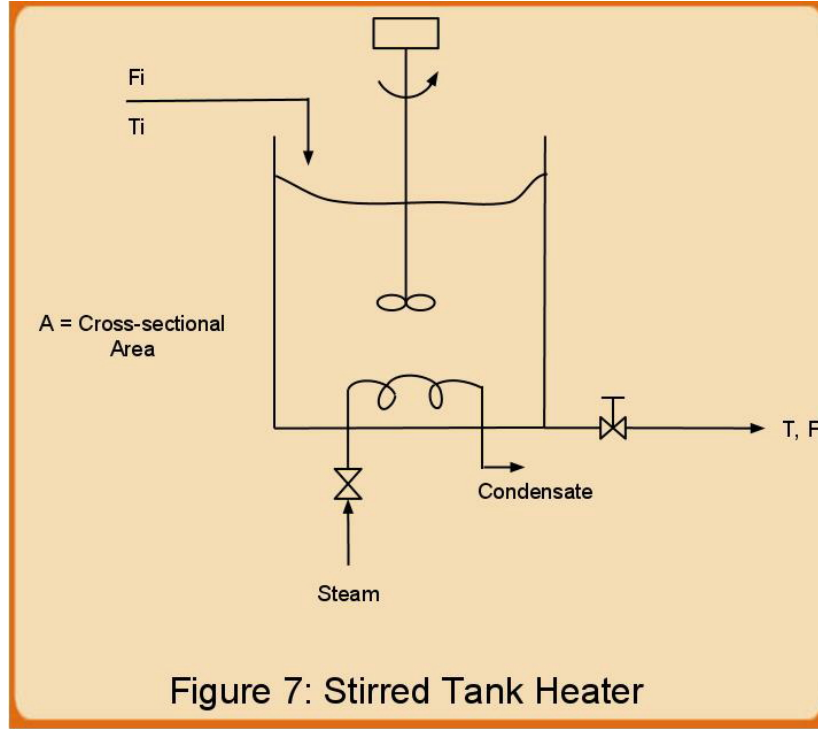
$$\frac{dE}{dt} = \frac{d(U + K + P)}{dt} = \sum \rho_i F_i h_i - \sum \rho_j F_j h_j \pm Q \pm W_s \simeq \frac{dH}{dt}$$

Variables and parameters appearing in these equations are described in Table 3.

By convention, a quantity is considered positive if it flows in and negative if it flows out. The state equations with the associated variables constitute a 'lumped parameter mathematical model' of a process, which yields the dynamic or static behavior of the process. The application of the conservation principle stated above will yield a set of differential equations with the fundamental quantities as the dependent variables and time as independent variable. The solution of the differential equations will determine how the state variables change with time i.e., it will determine the dynamic behavior of the process. The process is said to be at the steady state if the state variables do not change with time. In this case, the rate of accumulation of the fundamental quantity S is zero and the resulting balance yields a set of algebraic equations

Table 3: Description of Variables and Parameters

$i$	inlet
$j$	outlet
$\rho$	Density of the material in the system
$\rho_i$	Density of the material in the i'th inlet stream
$\rho_j$	Density of the material in the j'th outlet stream
$V$	Total volume of the system
$F_{i:}$	Volumetric flow rate of the i'th inlet stream
$F_{j:}$	Volumetric flow rate of the j'th outlet stream
$n_a$	Number of moles of the component A in the system
$C_A$	Molal concentration ( moles /volume)of A in the system
$C_{Ai}$	Molal concentration ( moles /volume)of A in the i'th inlet stream
$C_{Aj}$	Molal concentration ( moles /volume)of A in the j'th outlet stream
$r$	Reaction rate per unit volume of the component A in the system.
$h_i$	Specific enthalpy of the material in the i'th inlet stream
$h_j$	Specific enthalpy of the material in the j'th outlet stream
$U, K, P$	Internal, kinetic and potential energies of the system, respectively.
$Q$	Amount of the heat exchanged between the system and the surroundings per unit time
$W_S$	Shaft work exchanged between the system and its surroundings.



**Example 5 Stirred Tank Heater System (Figure 7):** Total momentum of the system remains constant and will not be considered. Total mass balance: Total mass in the tank at any time  $t = \rho V = \rho Ah$  where  $A$  represents cross sectional area.

$$\frac{d(\rho Ah)}{dt} = \rho F_i - \rho F \quad (31)$$

Assuming that the density is independent of the temperature,

$$A \frac{dh}{dt} = F_i - F \quad (32)$$

Now, flow out due to the gravity is also a function of height

$$F = k\sqrt{h}$$

Thus,

$$A \frac{dh}{dt} + k\sqrt{h} = F_i \quad (33)$$

Total energy of liquid in the tank is given by

$$E = U + K + P$$

However, since tank does not move

$$\frac{dK}{dt} = \frac{dP}{dt} = 0 ; \quad \frac{dE}{dt} = \frac{dU}{dt}$$

For liquid systems

$$\frac{dU}{dt} \approx \frac{dH}{dt} \quad (34)$$

where  $H$  is total enthalpy of the liquid in the tank.

$$H = \rho V C_p (T - T_{ref}) = \rho A h C_p (T - T_{ref}) \quad (35)$$

$T_{ref}$  represents reference temperature where the specific enthalpy of the liquid is assumed to be zero. Now, using the energy conservation principle

$$\frac{d(\rho A h C_p (T - T_{ref}))}{dt} = \rho F_i C_p (T_i - T_{ref}) - \rho F C_p (T - T_{ref}) + Q \quad (36)$$

where  $Q$  is the amount of heat supplied by the steam per unit time. Assuming  $T_{ref} = 0$ , we have

$$A \frac{d(hT)}{dt} = F_i T_i - FT + \frac{Q}{\rho C_p} \quad (37)$$

$$\begin{aligned} A \frac{d(hT)}{dt} &= Ah \frac{dT}{dt} + AT \frac{dh}{dt} \\ &= Ah \frac{dT}{dt} + T(F_i - F) \\ &= F_i T_i - FT + \frac{Q}{\rho C_p} \end{aligned}$$

Or

$$Ah \frac{dT}{dt} = F_i (T_i - T) + \frac{Q}{\rho C_p}$$

Summarizing modelling steps

$$\frac{dh}{dt} = \frac{1}{A} (F_i - F) = \frac{1}{A} (F_i - k\sqrt{h}) \quad (38)$$

$$\frac{dT}{dt} = \frac{F_i}{Ah} (T_i - T) + \frac{Q}{Ah\rho C_p} \quad (39)$$

The associated variables can be classified as

- **state**(or dependent) variables :  $h, T$
- **Input** (or independent) variables :  $T_i, F_i, Q$
- **Parameters**:  $A, \rho, C_p$

Steady state behavior can be computed by solving following two equations

$$\frac{dh}{dt} = F_i - k\sqrt{h} = 0 \quad (40)$$

$$\frac{dT}{dt} = \frac{F_i}{Ah}(T_i - T) + \frac{Q}{\rho C_p} = 0 \quad (41)$$

Once we choose independent variables  $F_i = \bar{F}_i$ ,  $T_i = \bar{T}_i$  and  $Q = \bar{Q}$ , the steady state  $h = \bar{h}$  and  $T = \bar{T}$  can be computed by simultaneously solving nonlinear algebraic equations (40-41).

The system will be disturbed from the steady state if the input variables suddenly change value at  $t = 0$ . Consider following two situations in which we need to investigate transient behavior of the above process

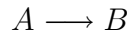
- $T_i$  decreases by 10% from its steady state value  $\bar{T}_i$  at  $t = 0$ . Liquid level remains at the same steady state value as  $T_i$  does not influence the total mass in tank. The temperature  $T$  in the tank will start decreasing with time (see Figure 8). How  $T(t)$  changes with time is determined by the solution of the equation (38) using the initial as condition  $T(0) = \bar{T}$ , the steady state value of  $T$ .
- $F_i$  is decreased by 10% from its steady state value  $\bar{F}_i$ : Since  $F_i$  appears in both the dynamic equations, the temperature and the liquid level will start changing simultaneously and the dynamics will be governed by simultaneous solution of coupled nonlinear differential equations (38-39) starting with initial conditions  $T(0) = \bar{T}$ ,  $h(0) = \bar{h}$ . Figure 9 show schematic diagrams of the process responses for step change in  $F_i$ .

It is also possible to investigate response of the system for more complex inputs, such as

$$T_i(t) = \bar{T}_i + \Delta T_i \sin(\omega t)$$

where above function captures daily variation of cooling water inlet temperature. In each case, the transient behavior  $T(t)$  and  $h(t)$  is computed by solving the system of ODEs subject to given initial conditions and time variation of independent inputs (i.e. forcing functions).

**Example 6** *Three isothermal CSTRs in series: Consider three isothermal CSTRs in series in which a first order liquid phase reaction of the form*



*is carried out. It is assumed that volume and liquid density remains constant in each tank and*

$$V_1 \frac{dC_{A1}}{dt} = F(C_{A0} - C_{A1}) - kV_1 C_{A1} \quad (42)$$



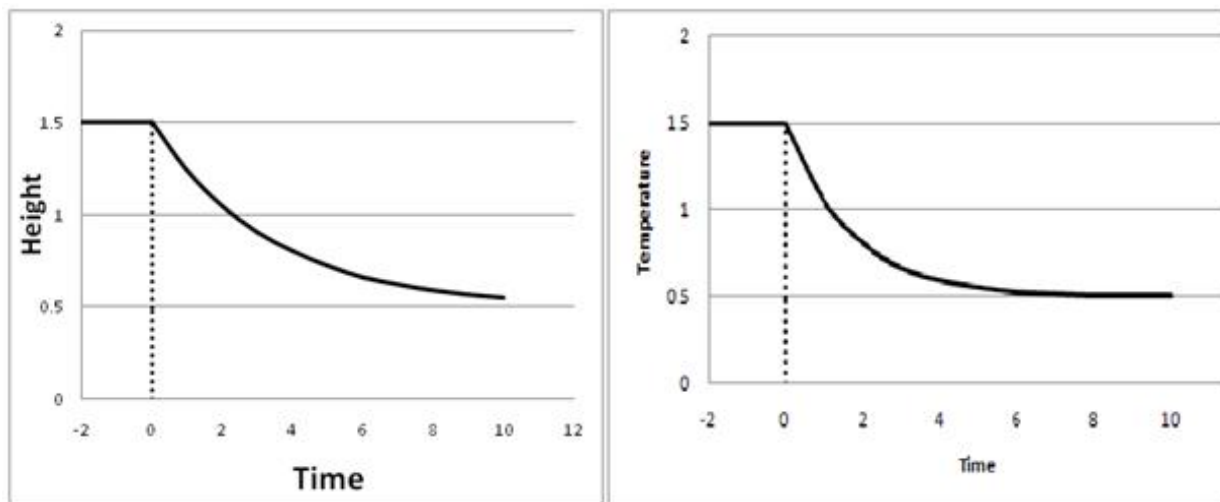
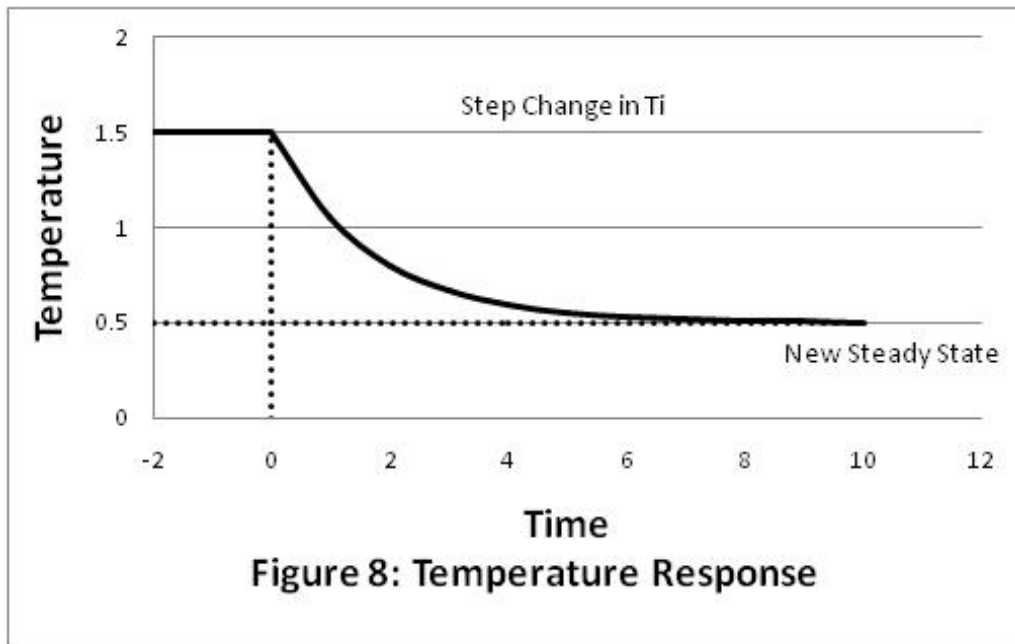


Figure 9: Dynamic Response to Step Change in  $F_i$

$$V_2 \frac{dC_{A2}}{dt} = F(C_{A1} - C_{A2}) - kV_2 C_{A2} \quad (43)$$

$$V_3 \frac{dC_{A3}}{dt} = F(C_{A2} - C_{A3}) - kV_3 C_{A3} \quad (44)$$

Defining  $\tau = F/V$ , we can rearrange the above set of equations as

$$\frac{d}{dt} \begin{bmatrix} C_{A1} \\ C_{A2} \\ C_{A3} \end{bmatrix} = \begin{bmatrix} -(k+1/\tau_1) & 0 & 0 \\ 1/\tau & -(k+1/\tau_2) & 0 \\ 0 & 1/\tau & -(k+1/\tau_3) \end{bmatrix} \begin{bmatrix} C_{A1} \\ C_{A2} \\ C_{A3} \end{bmatrix} + \begin{bmatrix} 1/\tau_1 \\ 0 \\ 0 \end{bmatrix} C_{A0} \quad (45)$$

$$\begin{aligned} \mathbf{x} &= [C_{A1}, C_{A2}, C_{A3}]^T \\ \frac{d\mathbf{x}}{dt} &= A\mathbf{x} + BC_{A0} \end{aligned} \quad (46)$$

where matrices  $A$  and  $B$  are defined in the above equation. Now, suppose initially  $C_{A0} = \bar{C}_{A0}$ , till  $t = 0$ , and, for  $t \geq 0$ ,  $C_{A0}$  was changed to  $C_{A0} = 0$ . Then we are required to solve

$$\frac{d\mathbf{x}}{dt} = A\mathbf{x}; \quad \mathbf{x} = \mathbf{x}(0) \quad \text{at} \quad t = 0 \quad (47)$$

and generate trajectories  $\mathbf{x}(t)$  (i.e.  $C_{A1}(t)$ ,  $C_{A2}(t)$  and  $C_{A3}(t)$ ) over interval  $[0, t_f]$ . This is a typical problem of dynamic simulation of lumped parameter system.

**Example 7 Continuous Fermenter:** Consider a continuously operated fermenter described by the following set of ODEs

$$\frac{dX}{dt} = F_1(X, S, P, D, S_f) = -DX + \mu X \quad (48)$$

$$\frac{dS}{dt} = F_2(X, S, P, D, S_f) = D(S_f - S) - \frac{1}{Y_{X/S}} \mu X \quad (49)$$

$$\frac{dP}{dt} = F_3(X, S, P, D, S_f) = -DP + (\alpha\mu + \beta)X \quad (50)$$

where  $X$  represents effluent cell-mass or biomass concentration,  $S$  represents substrate concentration and  $P$  denotes product concentration. It is assumed that product concentration ( $S$ ) and the cell-mass concentration ( $X$ ) are measured process outputs while dilution rate ( $D$ ) and the feed substrate concentration ( $S_f$ ) are process inputs which can be manipulated. Model parameter  $\mu$  represents the specific growth rate,  $Y_{X/S}$  represents the cell-mass yield,  $\alpha$  and  $\beta$  are the yield parameters for the product. The specific growth rate model is allowed to exhibit both substrate and product inhibition:

$$\mu = \frac{\mu_m(1 - \frac{P}{P_m})S}{K_m + S + \frac{S^2}{K_i}} \quad (51)$$

where  $\mu_m$  represents maximum specific growth rate,  $P_m$  represents product saturation constant,  $K_m$  substrate saturation constant and the  $K_i$  represents substrate inhibition constant. Defining state and input vectors as

$$\mathbf{x} = \begin{bmatrix} X & S & P \end{bmatrix}^T \quad ; \quad \mathbf{u} = \begin{bmatrix} D & S_f \end{bmatrix}^T \quad (52)$$

the above equation can be represented as

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x}, \mathbf{u}) \quad (53)$$

A typical problem dynamic simulation problem is to find trajectories of product, biomass and substrate concentrations over an interval  $[0, t_f]$ , given their initial values and dilution rate  $D(t)$  and feed substrate concentration  $S_f$  as a function of time over  $[0, t_f]$ .

In abstract terms, the dynamic simulation problem can be states as follows. Given time trajectories of independent variables  $\{\mathbf{u}(t) : 0 \leq t \leq t_f\}$ , and initial state,  $\mathbf{x}(0)$ , of the system, obtain state trajectories  $\{\mathbf{x}(t) : 0 \leq t \leq t_f\}$  by integrating

$$\frac{d\mathbf{x}}{dt} = F[\mathbf{x}(t), \mathbf{u}(t)] \quad ; \quad \mathbf{x} = \mathbf{x}(0) \text{ at } t = 0 \quad (54)$$

where  $\mathbf{x} \in R^n$  represents dependent or state variables and  $\mathbf{u} \in R^m$  denote independent inputs. As the independent variable trajectories are known *a-priori* while solving ODE-IVP, the problem can be looked at as  $n$ -ODE's in  $n$  variables with variable coefficients. Thus, the above problem can be re-stated as

$$\frac{d\mathbf{x}}{dt} = F_u(\mathbf{x}, t) \quad ; \quad \mathbf{x}(0) = \mathbf{x}_0 \quad (55)$$

In other words, a forced dynamic systems can be looked upon as unforced systems with variable parameters.

The model we considered above did not contain variation of the variables with respect to space. Such models are called as 'Lumped parameter models' and are described by ordinary differential equations of the form

$$\frac{dx_1}{dt} = f_1(x_1(t), x_2(t), \dots, x_n(t), u_1(t), u_2(t), \dots, u_m(t)) \quad (56)$$

$$\begin{aligned} & \dots\dots\dots \\ \frac{dx_n}{dt} &= f_n(x_1(t), x_2(t), \dots, x_n(t), u_1(t), u_2(t), \dots, u_m(t)) \quad (57) \\ x_1(0) &= \bar{x}_1, \dots, x_n(0) = \bar{x}_n \quad (\text{Initial conditions}) \end{aligned}$$

where  $x_1, \dots, x_n$  denote the state (or dependent) variables and  $u_1(t), \dots, u_n(t)$  are denote independent inputs (or forcing functions) specified for  $t \geq 0$ . Using vector notation, we can write the above set of ODEs in more compact form

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x}, \mathbf{u}) \quad (58)$$

$$\mathbf{x}(0) = \mathbf{x}_0 \quad (59)$$

where

$$\mathbf{x}(t) = [x_1(t) \dots x_n(t)]^T \in R^n \quad (60)$$

$$\mathbf{u}(t) = [u_1(t) \dots u_n(t)]^T \in R^n \quad (61)$$

$$F(\mathbf{x}, \mathbf{u}) = [f_1(\mathbf{x}, \mathbf{u}) \dots f_n(\mathbf{x}, \mathbf{u})]^T \in R^n \quad (62)$$

and  $\mathbf{u}(t)$  is a forcing function vector defined over  $t \geq 0$ .

- *Steady State Simulation Problem:* If we fix independent inputs to some constant value, say  $\mathbf{u}(t) = \bar{\mathbf{u}}$  for  $t \geq 0$ , then we can find a steady state solution  $\mathbf{x} = \bar{\mathbf{x}}$  corresponding to these constant inputs by simultaneously solving  $n$  nonlinear algebraic equations

$$F(\mathbf{x}, \bar{\mathbf{u}}) = \bar{\mathbf{0}} \quad (63)$$

obtained by setting  $d\mathbf{x}/dt = \bar{\mathbf{0}}$  where  $\bar{\mathbf{0}}$  represents  $n \times 1$  zero vector.

- *Dynamic Simulation Problem:* Given input trajectories

$$\mathbf{u}(t) = [u_1(t) \quad u_2(t) \dots u_m(t)]^T \quad (64)$$

as a function of time for  $t \geq 0$  and with the initial state  $\mathbf{x}(0)$ , integrate

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x}, \mathbf{u}(t)) \quad (65)$$

over interval  $0 \leq t \leq t_f$  to determine state trajectories

$$\mathbf{x}(t) = [x_1(t) \quad x_2(t) \dots x_n(t)]^T \quad (66)$$

Since  $\mathbf{u}(t)$  is a known function of time, we re-state the above problem as

$$\frac{d\mathbf{x}}{dt} = F_{\mathbf{u}}(\mathbf{x}, t) \quad ; \quad \mathbf{x}(0) = \mathbf{x}_0 \quad (67)$$

$F_{\mathbf{u}}(\mathbf{x}, t) (= F(\mathbf{x}, \mathbf{u}(t)))$  denotes  $F()$  with the given  $\mathbf{u}(t)$ .

Table 4: pH Balance Problem: Parameters and Initial Conditions

Parameter	Value
Equilibrium constant for water Kw	$10^{-14}$
Relative strength of acid mixture in the CSTR Ka	0.001
Feed rate to the tank F	13 L/min
Flow rate of the base m	15 L/min
Concentration of the base solution Cr	1 equiv/L
Concentration of the acid and its salts U	0.13 mol/L
Volume of tank V	90 L
Variable	Initial Value
$N^+$	0.005
$H^+$	0.086
$\hat{N}^+$	0.01
$\hat{H}^+$	0.0068

### 3 Differential Algebraic Equations

Another important class of problems that arise in process engineering is a set of coupled differential algebraic equations. In this section, we discuss two examples belonging to this class.

**Example 8** *The process is a continuously stirred tank reactor, where a feed with unknown pH is flowing into the reactor. We add a basic solution, with known molarity, to the reactor to maintain the pH at a desired level. The flow-rate of the basic solution is the manipulated variable. The process is modelled using the following set of DAEs:-*

$$\frac{VdN^+}{dt} = m \times Cr - (F + m)N^+ \quad (68)$$

$$\begin{aligned} &[H^+]^3 + (Ka + N^+)[H^+]^2 + \\ &(N^+Ka - Kw - KaU)H^+ - KaKw = 0 \end{aligned} \quad (69)$$

where  $N^+$  is the concentration of the cation of the base in the CSTR and is the differential state, while hydrogen ion concentration,  $(H^+)$ , is the algebraic state. The parameters and initial conditions are summarized in Table 4.

**Example 9** *The system presented here models the galvanostatic charge process of a thin film nickel hydroxide electrode. The rate of change of the mole fraction of nickel hydroxide*

is  $(y_1)$  given by

$$\frac{\rho V}{W} \frac{dy_1}{dt} = \frac{j_1}{F} \quad (70)$$

$$j_1 + j_2 - i_{app} = 0 \quad (71)$$

where

$$\begin{aligned} j_1 = & i_{o1} [2(1 - y_1) \exp(\frac{0.5F}{RT}(y_2 - \Phi_{eq,1})) - 2y_1 \\ & \times \exp(\frac{-0.5F}{RT}(y_2 - \Phi_{eq,1}))] \end{aligned} \quad (72)$$

$$j_2 = i_{o2} [\exp(\frac{F}{RT}(y_2 - \Phi_{eq,2})) - \exp(\frac{-F}{RT}(y_2 - \Phi_{eq,2}))] \quad (73)$$

where  $y_2$  is the potential difference at the solid liquid interface. (70) is the species balance while (71) denotes the charge balance.  $j_1$  and  $j_2$  are derived from Butler-Volmer kinetics. The parameters and initial condition values are summarized in Table 5.

Table 5: Ni-H electrode problem: Parameters and Initial Conditions

Parameter	Value
Faraday's Constant F	96487 C/mol
Ideal Gas Constant R	8.314 J/molK
Temperature T	298.15 K
equilibrium potential for nickel reaction $\Phi_{eq,1}$	0.420 V
equilibrium potential for oxygen reaction $\Phi_{eq,2}$	0.303 V
Density of nickel $\rho$	3.4g/cm <sup>3</sup>
Molecular Weight W	92.7 g/mol
effective length V	1 × 10 <sup>-5</sup> cm
applied current density on nickel electrode $i_{app}$	1 × 10 <sup>-5</sup> A/cm <sup>2</sup>
exchange current density of nickel reaction $i_{o1}$	1 × 10 <sup>-4</sup> A/cm <sup>2</sup>
exchange current density of oxygen reaction $i_{o2}$	1 × 10 <sup>-8</sup> A/cm <sup>2</sup>
Variable	Initial Value
$y_1$	0.35024
$y_2$	0.4074
$\hat{y}_1$	0.5322
$\hat{y}_2$	0.4254

A general nonlinear DAE system of equations, which are often encountered in process applications, can be described by the following general form of coupled differential and

algebraic equations

$$\begin{aligned}\frac{d\mathbf{x}(t)}{dt} &= \mathbf{f}(\mathbf{x}, \mathbf{z}, \mathbf{u}) \\ \mathbf{g}(\mathbf{x}, \mathbf{z}, \mathbf{u}) &= \bar{\mathbf{0}}\end{aligned}\tag{74}$$

$\mathbf{x} \in \mathbb{R}^{n_d}$  are the differential states of the process,  $\mathbf{z} \in \mathbb{R}^{n_a}$  are the algebraic states of the process and  $\mathbf{u} \in \mathbb{R}^u$  are the input variables. It is important to note that the initial condition,  $\mathbf{x}(0) = \mathbf{x}_0$ , in this case has to be consistent with  $\mathbf{z}(0) = \mathbf{z}_0$ , such that the algebraic constraints are satisfied

$$\mathbf{g}(\mathbf{x}_0, \mathbf{z}_0, \mathbf{u}(0)) = \bar{\mathbf{0}}$$

This class of problems need separate treatment while developing numerical solution schemes.

### 3.1 Partial Differential Equations (PDEs) and ODE-Boundary value Problems (ODE-BVP)

Most of the systems encountered in chemical engineering are distributed parameter systems. Even though behavior of some of these systems can be adequately represented by lumped parameter models, such simplifying assumptions may fail to provide accurate picture of system behavior in many situations and variations of variables along time and space have to be considered while modeling. This typically results in a set of partial differential equations.

**Example 10** Consider the double pipe heat exchanger in which a liquid flowing in the inner tube is heated by steam flowing countercurrently around the tube (Figure 10). The temperature in the pipe changes not only with time but also along the axial direction  $z$ . While developing the model, it is assumed that the temperature does not change along the radius of the pipe. Consequently, we have only two independent variables, i.e.  $z$  and  $t$ . To perform the energy balance, we consider an element of length  $\Delta z$  as shown in the figure. For this element, over a period of time  $\Delta t$

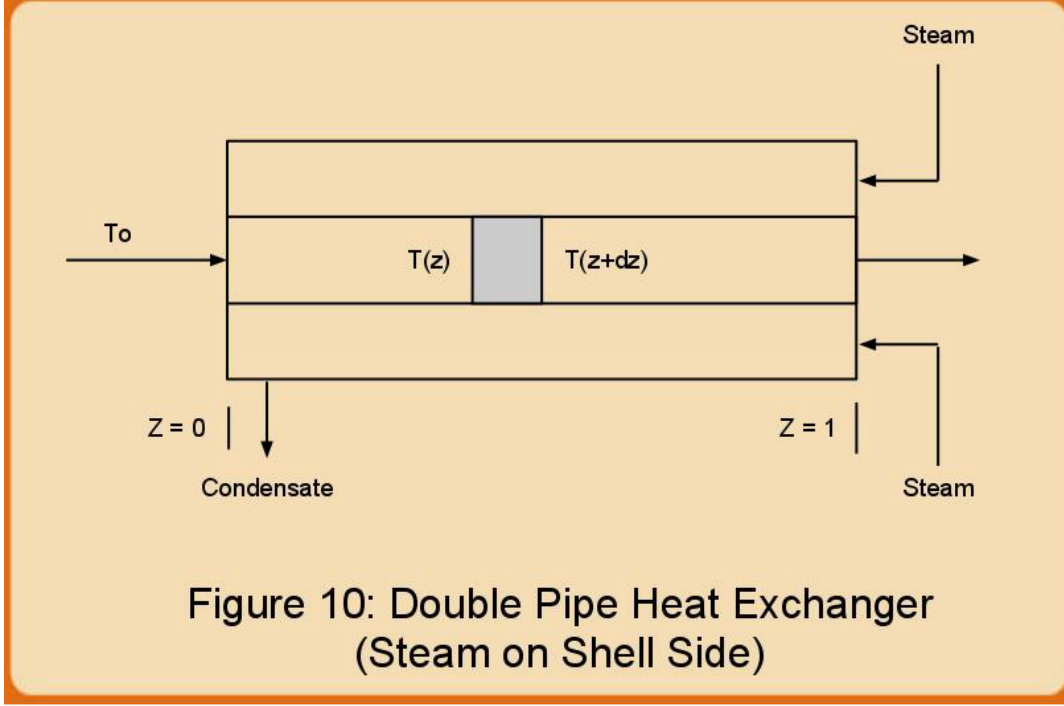
$$\rho C_p A \Delta z [(T)_{t+\Delta t} - (T)_t] = \rho C_p V A (T)_z \Delta t - \rho C_p V A (T)_{z+\Delta z} \Delta t + Q \Delta t (\pi D \Delta z) \tag{75}$$

This equation can be explained as

$$\begin{aligned}& [\text{accumulation of the enthalpy during the time period } \Delta t] \\ &= [\text{flow in of the enthalpy during } \Delta t] - [\text{flow out of the enthalpy during } \Delta t] \\ & [\text{enthalpy transferred from steam to the liquid through wall during } \Delta t]\end{aligned}$$

where

$Q$  : amount of heat transferred from the steam to the liquid per unit time and per unit heat transfer area.



$A$  : cross section area of the inner tube.

$V$  : average velocity of the liquid (assumed constant).

$D$  : external diameter of the inner tube.

Dividing both the sides by  $(\Delta z \Delta t)$  and taking limit as  $\Delta t \rightarrow 0$  and  $\Delta z \rightarrow 0$ , we have

$$\rho C_p A \frac{\partial T(z, t)}{\partial t} = -\rho C_p V A \frac{\partial T(z, t)}{\partial z} + \pi D Q \quad (76)$$

$$Q = U[T_{st} - T] \quad (77)$$

Boundary conditions:

$$T(t, z = 0) = T_1 \text{ for } t \geq 0$$

Initial condition

$$T(t = 0, z) = T_0(0, z) \quad (78)$$

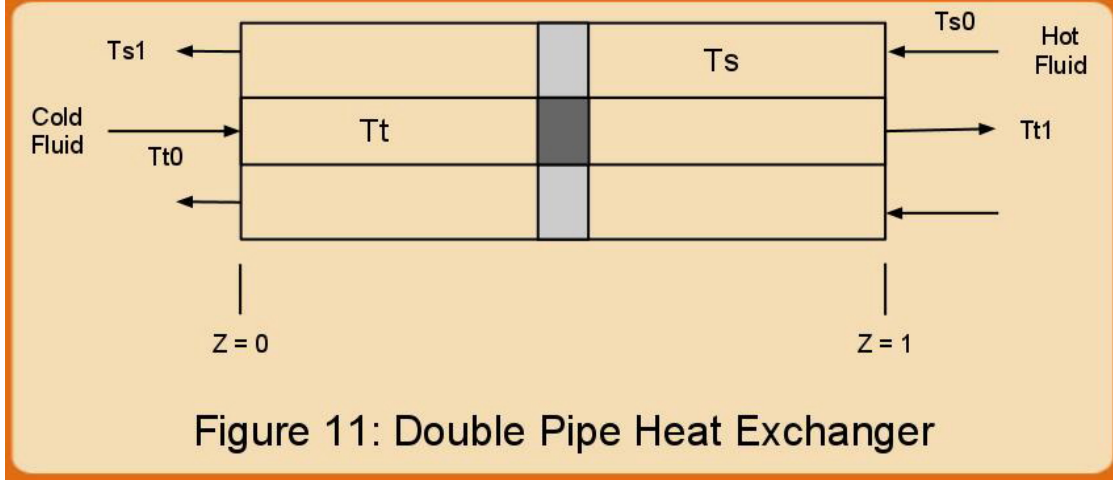
**Steady State Simulation:** Find  $T(z)$  given  $T(z = 0) = T_1$  when  $\partial T / \partial t = 0$ , i.e. solve for

$$\rho C_p V A \frac{\partial T}{\partial z} = \pi D Q = \pi D Q U (T_{st} - T) \quad (79)$$

$$T(0) = T_1 \quad (80)$$

This results in a ODE-IVP, which can be solved to obtain steady state profiles  $T(z)$  for specified heat load and liquid velocity.





### Dynamic Simulation

$$\rho C_p A \frac{\partial T}{\partial t} = -\rho C_p V A \frac{\partial T}{\partial z} + \pi D Q \quad (81)$$

with

$$T(t, 0) = T_1 \text{ at } z = 0 \text{ and } t \geq 0 : \text{ Boundary condition} \quad (82)$$

$$T(0, z) = T_0(z) : \text{ Initial temperature profile} \quad (83)$$

This results in a Partial Differential Equation (PDE) model for the distributed parameter system.

**Example 11** Now, let us consider the situation where the some hot liquid is used on the shell side to heat the tube side fluid (see Figure 11). The model equations for this case can be stated as

$$\rho_t C_{pt} A_t \frac{\partial T_t(z, t)}{\partial t} = -\rho_t C_{pt} V_t A_t \frac{\partial T_t(z, t)}{\partial z} + \pi D Q(z, t) \quad (84)$$

$$\rho_s C_{ps} A_s \frac{\partial T_s(z, t)}{\partial t} = \rho_s C_{ps} V_s A_s \frac{\partial T_s(z, t)}{\partial z} - \pi D Q(z, t) \quad (85)$$

$$Q(z, t) = U[T_s(z, t) - T_t(z, t)] \quad (86)$$

where subscript  $t$  denotes tube side and subscript  $s$  denotes shell side. The initial and boundary conditions become

$$T_t(t, 0) = T_{t0} \text{ at } z = 0 \text{ and } t \geq 0 : \text{ Boundary condition} \quad (87)$$

$$T(0, z) = T_{t0}(z) : \text{ Initial temperature profile} \quad (88)$$

$$T_s(t, 1) = T_{s1} \text{ at } z = 1 \text{ and } t \succeq 0 : \text{ Boundary condition} \quad (89)$$

$$T(0, z) = T_{s0}(z) : \text{ Initial temperature profile} \quad (90)$$

These are coupled PDEs and have to be solved simultaneously to understand the transient behavior. The steady state problem can be stated as

$$\rho_t C_{pt} V_t A_t \frac{dT_t(z, t)}{dz} = \pi DU [T_s(z) - T_t(z)] \quad (91)$$

$$\rho_s C_{ps} V_s A_s \frac{dT_s(z, t)}{dz} = \pi DU [T_s(z) - T_t(z)] \quad (92)$$

$$T_t(0) = T_{t0} \text{ at } z = 0 \quad (93)$$

$$T_s(1) = T_{s1} \text{ at } z = 1 \quad (94)$$

Equations (91-92) represent coupled ordinary differential equations. The need to compute steady state profiles for the counter-current double pipe heat exchanger results in a boundary value problem (ODE-BVP) as one variable is specified at  $z = 0$  while the other is specified at  $z = 1$ .

Before we conclude this section, we briefly review some terminology associated with PDEs, which will be used in the later modules.

**Definition 12 Order of PDE:** Order of a PDE is highest order of derivative occurring in PDE.

**Definition 13 Degree of PDE:** Power to which highest order derivative is raised.

**Example 14** Consider PDE

$$\partial u / \partial t + (d^2 u / dz^2)^n = u^3 \quad (95)$$

Here, the *Order* = 2 and *Degree* =  $n$ . Solutions of PDEs are sought such that it is satisfied in the domain and on the boundaries. A problem is said to be well posed when the solution is uniquely determined and it is sufficiently smooth and differentiable function of the independent variables. The boundary conditions have to be consistent with one another in order for a problem to be well posed. This implies that at the points common to boundaries, the conditions should not violate each other.

A linear PDE can be classified as:

- **Homogeneous equations:** Differential equation that does not contain any terms other than dependent variables and their derivatives.

$$\partial u / \partial t = \partial^2 u / \partial x^2 \quad (96)$$

$$\partial^2 u / \partial x^2 + \partial^2 u / \partial y^2 = 0$$

- Non homogeneous equations: Contain terms other than dependent variables

$$\partial u / \partial t = \partial^2 u / \partial x^2 + \sin x \quad (97)$$

$$\partial^2 u / \partial x^2 + \partial^2 u / \partial y^2 = \sin x \sin y \quad (98)$$

Similarly, the boundary conditions can be homogeneous or non homogeneous depending on whether they contain terms independent of dependent variables.

The PDEs typically encountered in engineering applications are  $2^{nd}$  order PDEs (reaction-diffusion systems, heat transfer, fluid-flow etc.)

### Classification of $2^{nd}$ order PDEs:

Consider a  $2^{nd}$  order PDE in  $n$  independent variables  $(x_1, x_2, x_3, x_4) = (x, y, z, t)$ . This can be written as

$$\sum_{i=1}^4 \sum_{j=1}^4 a_{ij} \frac{\partial^2 u}{\partial x_i \partial x_j} = f [\partial u / \partial x_1, \dots, \partial u / \partial x_4, u, x_1, \dots, x_4] \quad (99)$$

$a_{ij}$  are assumed to be independent of  $u$  and its derivative. They can be functions of  $(x_i)$ .  $a_{ij}$  can always be written as  $a_{ij} = a_{ji}$  for  $i \neq j$  as

$$\frac{\partial^2 u}{\partial x_i \partial x_j} = \frac{\partial^2 u}{\partial x_j \partial x_i} \quad (100)$$

Thus,  $a_{ij}$  are elements of a real symmetric matrix  $A$ . Obviously  $A$  has real eigen values. The PDE is called

- **Elliptic:** if all eigenvalues are +ve or -ve.
- **Hyperbolic:** if some eigenvalues are +ve and rest are -ve.
- **Parabolic:** if at-least one eigen value is zero.

The classification is global if  $a_{ij}$  are independent of  $x_i$ , else it is local. Typical partial differential equations we come across in engineering applications are of the form

$$\nabla^2 u = a \frac{\partial u}{\partial t} + b \frac{\partial^2 u}{\partial t^2} + cu + f(x_1, x_2, x_3, t) \quad (101)$$

subject to appropriate boundary conditions and initial conditions. This PDE is solved in a three dimensional region  $V$ , which can be bounded or unbounded. The boundary of  $V$  is denoted by  $S$ . On the spatial surface  $S$ , we have boundary conditions of the form

$$(\alpha(s, t) \hat{n}) \cdot \nabla u + \beta(s, t)u = h(s, t) \quad (102)$$

where  $\hat{n}$  is the outward normal direction to  $S$  and  $s$  represents spatial coordinate along  $S$ . We can classify the PDEs as follows

- Elliptic:  $a = b = 0$
- Parabolic:  $a \neq 0, b = 0$
- Hyperbolic:  $b > 0$

Elliptic Problems typically arise while studying steady-state behavior of diffusive systems. Parabolic or hyperbolic problems typically arise when studying transient behavior of diffusive systems.

## 4 Summary

This module introduces different basic forms of equations through examples of steady state and dynamic models of simple unit operations in chemical processing. The following abstract equation forms / formulations have been identified

- Linear algebraic equations
- Nonlinear algebraic equations
- Optimization based estimation / formulations
- Ordinary Differential Equations : Initial Value Problem (ODE-IVP)
- Differential Algebraic Equations (DAE)
- Ordinary Differential Equations : Boundary Value Problem (ODE-BVP)

- Partial Differential Equations (PDEs)

Methods for dealing with numerical solutions of these abstract equation forms / formulations will be discussed in the subsequent modules.