

Chapter 2: Examples of Mathematical Models for Chemical Processes

In this chapter we develop mathematical models for a number of elementary chemical processes that are commonly encountered in practice. We will apply the methodology discussed in the previous chapter to guide the reader through various examples. The goal is to give the reader a methodology to tackle more complicated processes that are not covered in this chapter and that can be found in books listed in the reference. The organization of this chapter includes examples of systems that can be described by ordinary differential equations (ODE), i.e. lumped parameter systems followed by examples of distributed parameters systems, i.e. those described by partial differential equations (PDE). The examples cover both homogeneous and heterogeneous systems. Ordinary differential equations (ODE) are easier to solve and are reduced to simple algebraic equations at steady state. The solution of partial differential equations (PDE) on the other hand is a more difficult task. But we will be interested in the cases where PDE's are reduced to ODE's. This is naturally the case where under appropriate assumptions, the PDE's is a one-dimensional equation at steady state conditions. It is worth to recall, as noted in the previous chapters, that the distinction between lumped and distributed parameter models depends sometimes on the assumptions put forward by the modeler. Systems that are normally distributed parameter can be modeled under appropriate assumptions as lumped parameter systems. This chapter includes some examples of this situation.

2.1 Examples of Lumped Parameter Systems

2.1.1 Liquid Storage Tank

Consider the perfectly mixed storage tank shown in figure 2.1. Liquid stream with volumetric rate F_f (m^3/s) and density ρ_f flow into the tank. The outlet stream has volumetric rate F_o and density ρ_o . Our objective is to develop a model for the variations of the tank holdup, i.e. volume of the tank. The system is therefore the liquid in the tank. We will assume that it is perfectly mixed and that the density of the effluent is the same as that of tank content. We will also assume that the tank is isothermal, i.e. no variations in the temperature. To model the tank we need only to write a mass balance equation.

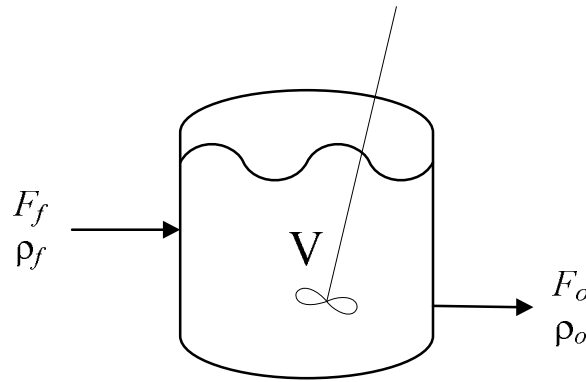


Figure 2-1 Liquid Storage Tank

Since the system is perfectly mixed, the system properties do not vary with position inside the tank. The only variations are with time. The mass balance equation can be written then on the whole system and not only on a differential element of it. This leads to therefore to a macroscopic model.

We apply the general balance equation (Eq. 1.2), to the total mass $m = \rho V$. This yields:

Mass flow in:

$$\rho_f F_f \quad (2.1)$$

Mass flow out:

$$\rho_o F_o \quad (2.2)$$

Accumulation:

$$\frac{dm}{dt} = \frac{d(\rho V)}{dt} \quad (2.3)$$

The generation term is zero since the mass is conserved. The balance equation yields:

$$\rho_f F_f = \rho_o F_o + \frac{d(\rho V)}{dt} \quad (2.4)$$

For consistency we can check that all the terms in the equation have the SI unit of kg/s. The resulting model (Eq. 2.4) is an ordinary differential equation (ODE) of first order where time (t) is the only independent variable. This is therefore a lumped parameter model. To solve it we need one initial condition that gives the value of the volume at initial time t_i , i.e.

$$V(t_i) = V_i \quad (2.5)$$

Under isothermal conditions we can further assume that the density of the liquid is constant i.e. $\rho_f = \rho_o = \rho$. In this case Eq. 2.4 is reduced to:

$$\frac{dV}{dt} = F_f - F_o \quad (2.6)$$

The volume V is related to the height of the tank L and to the cross sectional area A by:

$$V = AL \quad (2.7)$$

Since (A) is constant then we obtain the equation in terms of the state variable L :

$$A \frac{dL}{dt} = F_f - F_o \quad (2.8)$$

with initial condition:

$$L(t_i) = L_i \quad (2.9)$$

Degree of freedom analysis

For the system described by Eq. 2.8 we have the following information:

- Parameter of constant values: A
- Variables which values can be externally fixed (Forced variable): F_f
- Remaining variables: L and F_o
- Number of equations: 1 (Eq. 2.8)

Therefore the degree of freedom is:

$$\text{Number of remaining variables} - \text{Number of equations} = 2 - 1 = 1$$

For the system to be exactly specified we need therefore one more equations. This extra relation is obtained from practical engineering considerations. If the system is operated without control (at open loop) then the outlet flow rate F_o is a function of the liquid level L . Generally a relation of the form:

$$F_o = \alpha \sqrt{L} \quad (2.10)$$

could be used, where α is the discharge coefficient.

If on the other hand the liquid level is under control, then its value is kept constant at certain desired value L_s . If F_o is used to control the height then a control law relates F_o to L and L_s :

$$F_o = F_o(L, L_s) \quad (2.11)$$

For instant, if a proportional controller K_c is used then the control law is given by:

$$F_o = K_c(L - L_s) + F_{ob} \quad (2.12)$$

Where F_{ob} the bias, i.e. the constant value of F_o when the level is at the desired value i.e., $L = L_s$.

Note that at steady state, the accumulation term is zero (height does not change with time), i.e., $dL/dt = 0$. The model of the tank is reduced to the simple algebraic equation:

$$F_0 = F_f \quad (2.13)$$

2.1.2 Stirred Tank Heater

We consider the liquid tank of the last example but at non-isothermal conditions. The liquid enters the tank with a flow rate F_f (m^3/s), density ρ_f (kg/m^3) and temperature T_f (K). It is heated with an external heat supply of temperature T_{st} (K), assumed constant. The effluent stream is of flow rate F_o (m^3/s), density ρ_o (kg/m^3) and temperature T (K) (Fig. 2.2). Our objective is to model both the variation of liquid level and its temperature. As in the previous example we carry out a macroscopic model over the whole system. Assuming that the variations of temperature are not as large as to affect the density then the mass balance of Eq. 2.8 remains valid.

To describe the variations of the temperature we need to write an energy balance equation. In the following we develop the energy balance for any macroscopic system (Fig. 2.3) and then we apply it to our example of stirred tank heater.

The energy $E(J)$ of any system of (Fig. 2.3) is the sum of its internal $U(J)$, kinetic $K(J)$ and potential energy $\phi(J)$:

$$E = U + K + \phi \quad (2.14)$$

Consequently, the flow of energy into the system is:

$$\rho_f F_f (\tilde{U}_f + \tilde{K}_f + \tilde{\Phi}_f) \quad (2.15)$$

where the $(\tilde{\bullet})$ denotes the specific energy (J/kg).

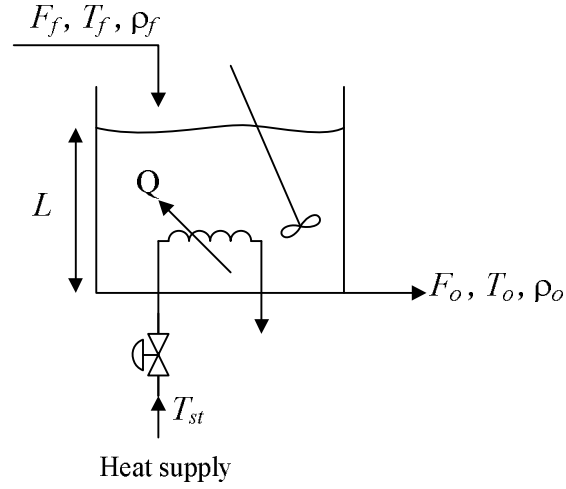


Figure 2-2 Stirred Tank Heater

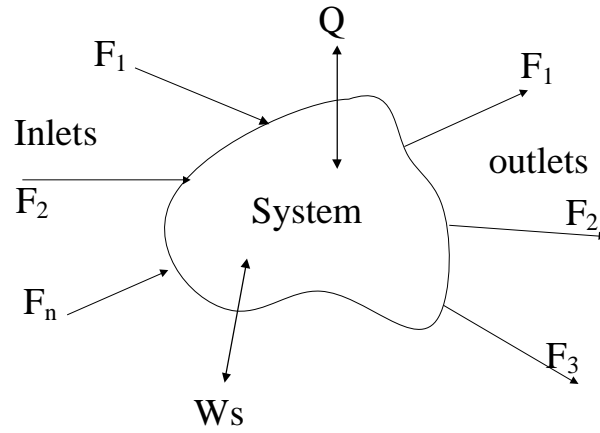


Figure 2-3 General Macroscopic System

The flow of energy out of the system is:

$$\rho_o F_o (\tilde{U}_o + \tilde{K}_o + \tilde{\Phi}_o) \quad (2.16)$$

The rate of accumulation of energy is:

$$\frac{d(\rho V(\tilde{U} + \tilde{K} + \tilde{\Phi}))}{dt} \quad (2.17)$$

As for the rate of generation of energy, it was mentioned in Section 1.8.4, that the energy exchanged between the system and the surroundings may include heat of reaction Q_r (J/s), heat exchanged with surroundings Q_e (J/s) and the rate of work done against pressure forces (flow work) W_{pv} (J/s), in addition to any other work W_o .

The flow of work W_{pv} done by the system is given by:

$$W_{pv} = F_o P_o - F_f P_f \quad (2.18)$$

where P_o and P_f are the inlet and outlet pressure, respectively.

In this case, the rate of energy generation is:

$$Q_e + Q_r - (W_o + F_o P_o - F_f P_f) \quad (2.19)$$

Substituting all these terms in the general balance equation (Eq. 1.7) yields:

$$\begin{aligned} \frac{d(\rho V(\tilde{U} + \tilde{K} + \tilde{\Phi}))}{dt} = & \rho_f F_f (\tilde{U}_f + \tilde{K}_f + \tilde{\Phi}_f) - \rho_o F_o (\tilde{U}_o + \tilde{K}_o + \tilde{\Phi}_o) \\ & + Q_e + Q_r - (W_o + F_o P_o - F_f P_f) \end{aligned} \quad (2.20)$$

We can check that all terms of this equation have the SI unit of (J/s). Equation (2.20)

can be also written as:

$$\begin{aligned} \frac{d(\rho V(\tilde{U} + \tilde{K} + \tilde{\Phi}))}{dt} = & \rho_f F_f (\tilde{U}_f + \tilde{K}_f + \tilde{\Phi}_f) - \rho_o F_o (\tilde{U}_o + \tilde{K}_o + \tilde{\Phi}_o) \\ & + Q_e + Q_r - W_o - F_o \rho_o \frac{P_o}{\rho_o} + F_f \rho_f \frac{P_f}{\rho_f} \end{aligned} \quad (2.21)$$

The term $\tilde{V} = 1/\rho$ is the specific volume (m^3/kg). Thus Eq. 2.21 can be written as:

$$\frac{d(\rho V(\tilde{U} + \tilde{K} + \tilde{\phi}))}{dt} = \rho_f F_f (\tilde{U}_f + P_f \tilde{V}_f + \tilde{K}_f + \tilde{\phi}_f) - \rho_o F_o (\tilde{U}_o + P_o \tilde{V}_o + \tilde{K}_o + \tilde{\phi}_o) + Q_e + Q_r - W_o \quad (2.22)$$

The term $\tilde{U} + P\tilde{V}$ that appears in the equation is the specific enthalpy \tilde{h} . Therefore, the general energy balance equation for a macroscopic system can be written as:

$$\frac{d(\rho V(\tilde{U} + \tilde{K} + \tilde{\phi}))}{dt} = \rho_f F_f (\tilde{h}_f + \tilde{K}_f + \tilde{\phi}_f) - \rho_o F_o (\tilde{h}_o + \tilde{K}_o + \tilde{\phi}_o) + Q_e + Q_r - W_o \quad (2.23)$$

We return now to the liquid stirred tank heater. A number of simplifying assumptions can be introduced:

- We can neglect kinetic energy unless the flow velocities are high.
- We can neglect the potential energy unless the flow difference between the inlet and outlet elevation is large.
- All the work other than flow work is neglected, i.e. $W_o = 0$.
- There is no reaction involved, i.e. $Q_r = 0$.

The energy balance (Eq. 2.23) is reduced to:

$$\frac{d(\rho V \tilde{U})}{dt} = \rho_f F_f \tilde{h}_f - \rho_o F_o \tilde{h}_o + Q_e \quad (2.24)$$

Here Q_e is the heat (J/s) supplied by the external source. Furthermore, as mentioned in Section 1.12, the internal energy \tilde{U} for liquids can be approximated by enthalpy, \tilde{h} . The enthalpy is generally a function of temperature, pressure and composition. However, it can be safely estimated from heat capacity relations as follows:

$$\tilde{h} = \tilde{C}_p(T - T_{ref}) \quad (2.25)$$

where \tilde{C}_p is the average heat capacity.

Furthermore since the tank is well mixed the effluent temperature T_o is equal to process temperature T . The energy balance equation can be written, assuming constant density $\rho_f = \rho_o = \rho$, as follows:

$$\rho \tilde{C}_p \frac{d(V(T - T_{ref}))}{dt} = \rho F_f \tilde{C}_p (T_f - T_{ref}) - \rho F_o \tilde{C}_p (T - T_{ref}) + Q_e \quad (2.26)$$

Taking $T_{ref} = 0$ for simplicity and since $V = AL$ result in:

$$\rho \tilde{C}_p A \frac{d(LT)}{dt} = \rho F_f \tilde{C}_p T_f - \rho F_o \tilde{C}_p T + Q_e \quad (2.27)$$

or equivalently:

$$A \frac{d(LT)}{dt} = F_f T_f - F_o T + \frac{Q_e}{\rho \tilde{C}_p} \quad (2.28)$$

Since

$$A \frac{d(LT)}{dt} = AT \frac{d(L)}{dt} + AL \frac{d(T)}{dt} \quad (2.29)$$

and using the mass balance (Eq. 2.8) we get:

$$AL \frac{dT}{dt} + T(F_f - F_o) = F_f T_f - F_o T + \frac{Q_e}{\rho \tilde{C}_p} \quad (2.30)$$

or equivalently:

$$AL \frac{dT}{dt} = F_f (T_f - T) + \frac{Q_e}{\rho \tilde{C}_p} \quad (2.31)$$

The stirred tank heater is modeled, then by the following coupled ODE's:

$$A \frac{dL}{dt} = F_f - F_o \quad (2.32)$$

$$AL \frac{dT}{dt} = F_f (T_f - T) + \frac{Q_e}{\rho \tilde{C}_p} \quad (2.33)$$

This system of ODE's can be solved if it is exactly specified and if conditions at initial time are known,

$$L(t_i) = L_i \quad \text{and} \quad T(t_i) = T_i \quad (2.34)$$

Degree of freedoms analysis

For this system we can make the following simple analysis:

- Parameter of constant values: A , ρ and C_p
- (Forced variable): F_f and T_f
- Remaining variables: L , F_o , T , Q_e
- Number of equations: 2 (Eq. 2.32 and Eq. 2.33)

The degree of freedom is therefore, $4 - 2 = 2$. We still need two relations for our problem to be exactly specified. Similarly to the previous example, if the system is operated without control then F_o is related to L through (Eq. 2.10). One additional relation is obtained from the heat transfer relation that specifies the amount of heat supplied:

$$Q_e = UA_H (T_{st} - T) \quad (2.35)$$

U and A_H are heat transfer coefficient and heat transfer area. The source temperature T_{st} was assumed to be known. If on the other hand both the height and temperature are under control, i.e. kept constant at desired values of L_s and T_s then there are two control laws that relate respectively F_o to L and L_s and Q_e to T and T_s :

$$F_o = F_o(L, L_s), \text{ and } Q_e = Q_e(T, T_s) \quad (2.36)$$

2.1.3 Isothermal CSTR

We revisit the perfectly mixed tank of the first example but where a liquid phase chemical reactions taking place:



The reaction is assumed to be irreversible and of first order. As shown in figure 2.4, the feed enters the reactor with volumetric rate F_f (m^3/s), density ρ_f (kg/m^3) and concentration C_{Af} ($mole/m^3$). The output comes out of the reactor at volumetric rate F_o , density ρ_o and concentration C_{Ao} ($mole/m^3$) and C_{Bo} ($mole/m^3$). We assume isothermal conditions.

Our objective is to develop a model for the variation of the volume of the reactor and the concentration of species A and B . The assumptions of example 2.1.1 still hold and the total mass balance equation (Eq. 2.6) is therefore unchanged

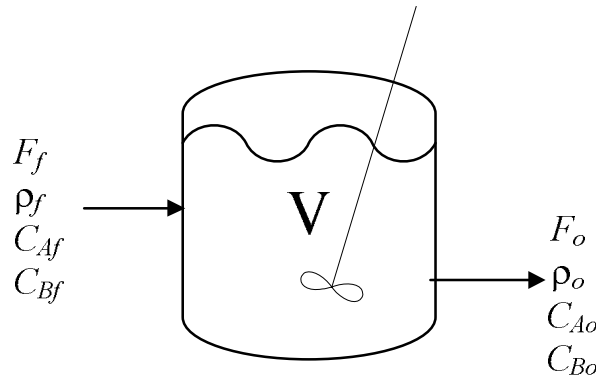


Figure 2.4 Isothermal CSTR

The component balance on species A is obtained by the application of (Eq. 1.3) to the number of moles ($n_A = C_A V$). Since the system is well mixed the effluent concentration C_{Ao} and C_{Bo} are equal to the process concentration C_A and C_B .

Flow of moles of A in:

$$F_f C_{Af} \quad (2.38)$$

Flow of moles of A out:

$$F_o C_{Ao} \quad (2.39)$$

Rate of accumulation:

$$\frac{dn}{dt} = \frac{d(VC_A)}{dt} \quad (2.40)$$

Rate of generation: $-rV$

where r (*moles/m³s*) is the rate of reaction.

Substituting these terms in the general equation (Eq. 1.3) yields:

$$\frac{d(VC_A)}{dt} = F_f C_{Af} - F_o C_A - rV \quad (2.41)$$

We can check that all terms in the equation have the unit (*mole/s*).

We could write a similar component balance on species B but it is not needed since it will not represent an independent equation. In fact, as a general rule, a system of n species is exactly specified by n independent equations. We can write either the total mass balance along with $(n - 1)$ component balance equations, or we can write n component balance equations.

Using the differential principles, equation (2.41) can be written as follows:

$$\frac{d(VC_A)}{dt} = V \frac{d(C_A)}{dt} + C_A \frac{d(V)}{dt} = F_f C_{Af} - F_o C_A - rV \quad (2.42)$$

Substituting Equation (2.6) into (2.42) and with some algebraic manipulations we obtain:

$$V \frac{d(C_A)}{dt} = F_f (C_{Af} - C_A) - rV \quad (2.43)$$

In order to fully define the model, we need to define the reaction rate which is for a first-order irreversible reaction:

$$r = k C_A \quad (2.44)$$

Equations 2.6 and 2.43 define the dynamic behavior of the reactor. They can be solved if the system is exactly specified and if the initial conditions are given:

$$V(t_i) = V_i \text{ and } C_A(t_i) = C_{Ai} \quad (2.45)$$

Degrees of freedom analysis

- Parameter of constant values: A
- (Forced variable): F_f and C_{Af}
- Remaining variables: V , F_o , and C_A
- Number of equations: 2 (Eq. 2.6 and Eq. 2.43)

The degree of freedom is therefore $3 - 2 = 1$. The extra relation is obtained by the relation between the effluent flow F_o and the level in open loop operation (Eq. 2.10) or in closed loop operation (Eq. 2.11).

The steady state behavior can be simply obtained by setting the accumulation terms to zero. Equation 2.6 and 2.43 become:

$$F_0 = F_f \quad (2.46)$$

$$F_f (C_{Af} - C_A) = rV \quad (2.47)$$

More complex situations can also be modeled in the same fashion. Consider the catalytic hydrogenation of ethylene:



where A represents hydrogen, B represents ethylene and P is the product (ethane). The reaction takes place in the CSTR shown in figure 2.5. Two streams are feeding the reactor. One concentrated feed with flow rate F_1 (m^3/s) and concentration C_{B1} ($mole/m^3$) and another dilute stream with flow rate F_2 (m^3/s) and concentration C_{B2} ($mole/m^3$). The effluent has flow rate F_o (m^3/s) and concentration C_B ($mole/m^3$). The reactant A is assumed to be in excess.

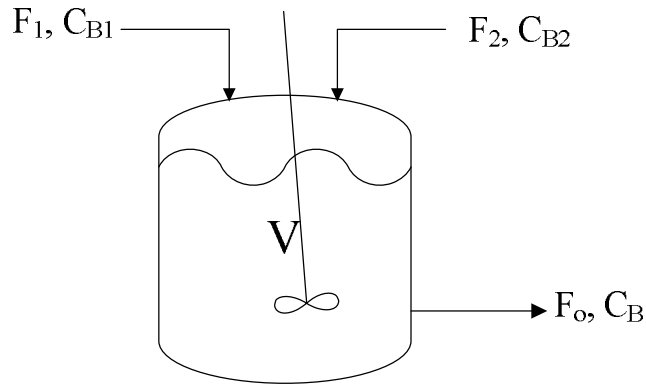


Figure 2-5 Reaction in a CSTR

The reaction rate is assumed to be:

$$r = \frac{k_1 C_B}{(1 + k_2 C_B)^2} \quad (mole/m^3.s) \quad (2.49)$$

where k_1 is the reaction rate constant and k_2 is the adsorption equilibrium constant. Assuming the operation to be isothermal and the density is constant, and following the same procedure of the previous example we get the following model:

Total mass balance:

$$A \frac{dL}{dt} = F_1 + F_2 - F_o \quad (2.50)$$

Component B balance:

$$V \frac{d(C_A)}{dt} = F_1(C_{B1} - C_B) + F_2(C_{B2} - C_B) - rV \quad (2.51)$$

Degrees of freedom analysis

- Parameter of constant values: A , k_1 and k_2
- (Forced variable): F_1 , F_2 , C_{B1} and C_{B2}
- Remaining variables: V , F_o , and C_B
- Number of equations: 2 (Eq. 2.50 and Eq. 2.51)

The degree of freedom is therefore $3 - 2 = 1$. The extra relation is between the effluent flow F_o and the level L as in the previous example.

2.1.4 Gas-Phase Pressurized CSTR

So far we have considered only liquid-phase reaction where density can be taken constant. To illustrate the effect of gas-phase chemical reaction on mass balance equation, we consider the following elementary reversible reaction:



taking place in perfectly mixed vessel sketched in figure 2.6. The influent to the vessel has volumetric rate F_f (m^3/s), density ρ_f (kg/m^3), and mole fraction y_f . Product comes out of the reactor with volumetric rate F_o , density ρ_o , and mole fraction y_o . The temperature

and volume inside the vessel are constant. The reactor effluent passes through control valve which regulate the gas pressure at constant pressure P_g .

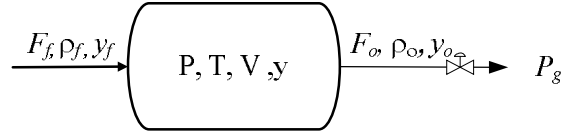


Figure 2-6 Gas Pressurized Reactor

Writing the macroscopic total mass balance around the vessel gives:

$$\frac{d(\rho V)}{dt} = \rho_f F_f - \rho_o F_o \quad (2.53)$$

Since V is constant we have:

$$V \frac{d\rho}{dt} = \rho_f F_f - \rho_o F_o \quad (2.54)$$

Writing the component balance, for fixed V , results in:

$$V \frac{dC_A}{dt} = F_f C_{Af} - F_o C_{Ao} - r_1 V + r_2 V \quad (2.55)$$

The reaction rates for the reversible reaction are assumed to be:

$$r_1 = k_1 C_A \quad (2.56)$$

$$r_2 = k_2 C_B^2 \quad (2.57)$$

Equations (2.54) and (2.55) define the variations of density and molar concentration. One can also rewrite the equation to define the behavior of the pressure (P) and mole

fraction (y). The concentration can be expressed in term of the density through ideal gas law:

$$C_A = yP/RT \quad (2.58)$$

$$C_B = (1 - y)P/RT \quad (2.59)$$

Similarly, the density can be related to the pressure using ideal gas law:

$$\rho = MP/RT = [M_A y + M_B (1 - y)]P/RT \quad (2.60)$$

Where M_A and M_B are the molecular weight of A and B respectively. Therefore one can substitute equations (2.58) to (2.60) into equations (2.54 & 2.55) in order to explicitly write the latter two equations in terms of y and P . Or, alternatively, one can solve all equations simultaneously.

Degrees of freedom analysis:

- Parameters: V, k_1, k_2, R, T, M_A and M_B
- Forcing function: F_f, C_{Af}, y_f
- Variables: C_A, C_B, y, P, ρ, F
- Number of equations: 5 (Eqs. 2.54, 2.55, 2.58, 2.59, 2.60)

The degree of freedom is therefore $6 - 5 = 1$. The extra relation relates the outlet flow to the pressure as follows:

$$F_o = C_v \sqrt{\frac{P - P_g}{\rho}} \quad (2.61)$$

where C_v is the valve-sizing coefficient. Recall also that P_g is assumed to be constant.

2.1.5 Non-Isothermal CSTR

We reconsider the previous CSTR example (Sec 2.1.3), but for non-isothermal conditions. The reaction $A \rightarrow B$ is exothermic and the heat generated in the reactor is

removed via a cooling system as shown in figure 2.7. The effluent temperature is different from the inlet temperature due to heat generation by the exothermic reaction.

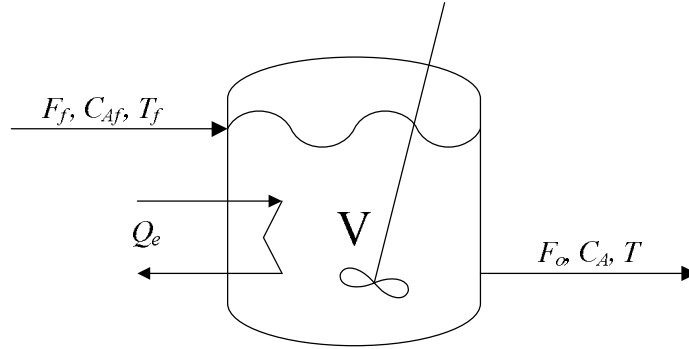


Figure 2-7 Non-isothermal CSTR

Assuming constant density, the macroscopic total mass balance (Eq. 2.6) and mass component balance (Eq. 2.43) remain the same as before. However, one more ODE will be produced from the applying the conservation law (equation 2.23) for total energy balance. The dependence of the rate constant on the temperature:

$$k = k_o e^{-E/RT} \quad (2.62)$$

should be emphasized.

The general energy balance (Eq. 2.23) for macroscopic systems applied to the CSTR yields, assuming constant density and average heat capacity:

$$\rho \tilde{C}_p \frac{d(V(T - T_{ref}))}{dt} = \rho F_f \tilde{C}_p (T_f - T_{ref}) - \rho F_o \tilde{C}_p (T - T_{ref}) + Q_r - Q_e \quad (2.63)$$

where Q_r (J/s) is the heat generated by the reaction, and Q_e (J/s) the rate of heat removed by the cooling system. Assuming $T_{ref} = 0$ for simplicity and using the differentiation principles, equation 2.63 can be written as follows:

$$\rho \tilde{C}_p V \frac{dT}{dt} + \rho \tilde{C}_p T \frac{dV}{dt} = \rho F_f \tilde{C}_p T_f - \rho F_o \tilde{C}_p T + Q_r - Q_e \quad (2.64)$$

Substituting Equation 2.6 into the last equation and rearranging yields:

$$\rho \tilde{C}_p V \frac{dT}{dt} = \rho F_f \tilde{C}_p (T_f - T) + Q_r - Q_e \quad (2.65)$$

The rate of heat exchanged Q_r due to reaction is given by:

$$Q_r = -(\Delta H_r) V r \quad (2.66)$$

where ΔH_r (J/mole) is the heat of reaction (has negative value for exothermic reaction and positive value for endothermic reaction). The non-isothermal CSTR is therefore modeled by three ODE's:

$$\frac{dV}{dt} = F_f - F_o \quad (2.67)$$

$$V \frac{d(C_A)}{dt} = F_f (C_{Af} - C_A) - rV \quad (2.68)$$

$$\rho \tilde{C}_p V \frac{dT}{dt} = \rho F_f \tilde{C}_p (T_f - T) + (-\Delta H_r) V r - Q_e \quad (2.69)$$

where the rate (r) is given by:

$$r = k_o e^{-E/RT} C_A \quad (2.70)$$

The system can be solved if the system is exactly specified and if the initial conditions are given:

$$V(t_i) = V_i \quad T(t_i) = T_i \quad \text{and} \quad C_A(t_i) = C_{Ai} \quad (2.71)$$

Degrees of freedom analysis

- Parameter of constant values: ρ , E , R , C_p , ΔH_r and k_o
- (Forced variable): F_f , C_{Af} and T_f

- Remaining variables: V, F_o, T, C_A and Q_e
- Number of equations: 3 (Eq. 2.67, 2.68 and 2.69)

The degree of freedom is $5-3 = 2$. Following the analysis of example 2.1.3, the two extra relations are between the effluent stream (F_o) and the volume (V) on one hand and between the rate of heat exchanged (Q_e) and temperature (T) on the other hand, in either open loop or closed loop operations.

A more elaborate model of the CSTR would include the dynamic of the cooling jacket (Fig. 2.8). Assuming the jacket to be perfectly mixed with constant volume V_j , density ρ_j and constant average thermal capacity Cp_j , the dynamic of the cooling jacket temperature can be modeled by simply applying the macroscopic energy balance on the whole jacket:

$$\rho_j \tilde{C}_{p_j} V_j \frac{dT_j}{dt} = \rho_j F_j \tilde{C}_{p_j} (T_{jf} - T_j) + Q_e \quad (2.72)$$

Since V_j , ρ_j , Cp_j and T_{jf} are constant or known, the addition of this equation introduces only one variable (T_j). The system is still exactly specified.

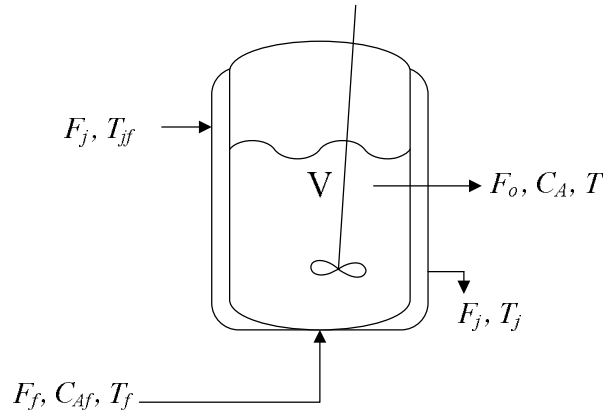


Figure 2-8 Jacketed Non-isothermal CSTR

2.1.6 Mixing Process

Consider the tank of figure 2.9 where two solutions 1 and 2 containing materials A and B are being mixed. Stream 1 has flow rate F_1 (m^3/s), density ρ_1 (kg/m^3), T_1 (K),

concentration C_{A1} (mole/m^3) and C_{B1} (mole/m^3) of material A and B. Similarly stream 2 has flow rate F_2 (m^3/s), density ρ_2 (kg/m^3), T_2 (K), concentration C_{A2} (mole/m^3) and C_{B2} (mole/m^3) of material A and B. The effluent stream has flow rate F_o (m^3/s), density ρ_o (kg/m^3), T_o (K), concentration C_{Ao} (mole/m^3) and C_{Bo} (mole/m^3) of material A and B. We assume that the mixing releases heat of rate Q (J/s) which is absorbed by a cooling fluid flowing in a jacket or a coil.

Our objective is to develop a model for the mixing process. We will assume that the tank is well mixed. In this case all the effluent properties are equal to the process properties. We also assume for simplicity that the densities and heat capacities of the streams are constant and equal:

$$\rho = \rho_1 = \rho_2 = \rho_o \quad (2.73)$$

$$Cp = Cp_1 = Cp_2 = Cp_3 \quad (2.74)$$

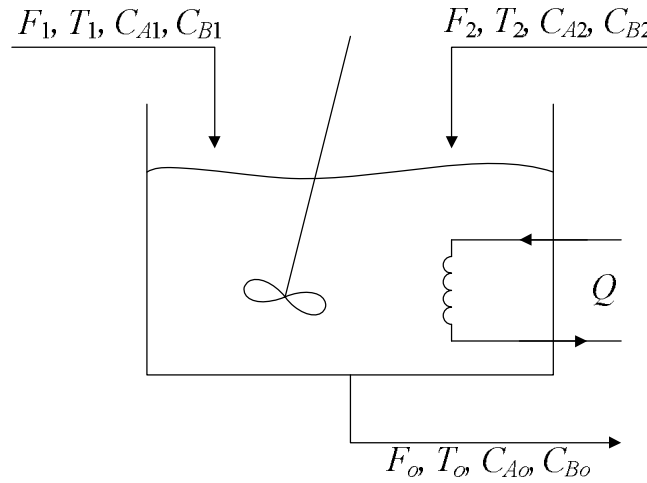


Figure 2-9 Mixing Process

Total mass balance

The mass balance equation yields

$$\frac{d(\rho V)}{dt} = (F_1 \rho_1 + F_2 \rho_2) - F_o \rho_o \quad (2.75)$$

Since the densities are equals we have:

$$\frac{dV}{dt} = (F_1 + F_2) - F_o \quad (2.76)$$

Component balance

The component balance for species A for instant yields:

$$\frac{d(\rho_o C_{Ao} V)}{dt} = (F_1 \rho_1 C_{A1} + F_2 \rho_2 C_{A2}) - F_o \rho_o C_{Ao} \quad (2.77)$$

Expanding Eq. 2.77 yields:

$$\rho_o \left(V \frac{dC_{Ao}}{dt} + C_{Ao} \frac{dV}{dt} \right) = (F_1 \rho_1 C_{A1} + F_2 \rho_2 C_{A2}) - F_o \rho_o C_{Ao} \quad (2.78)$$

Substituting Eq. 2.76 into 2.78 yields after some manipulation:

$$V \frac{dC_{Ao}}{dt} = F_1 (C_{A1} - C_{Ao}) + F_2 (C_{A2} - C_{Ao}) \quad (2.79)$$

A similar equation holds for component B,

$$\frac{d(\rho_o C_{Bo} V)}{dt} = (F_1 \rho_1 C_{B1} + F_2 \rho_2 C_{B2}) - F_o \rho_o C_{Bo} \quad (2.80)$$

Energy balance

The general energy balance equation (Eq. 2.23) yields, assuming negligible kinetic, potential energy and since no reaction or shaft work occurs:

$$\frac{d(\rho_o V \tilde{h}_{o,mix})}{dt} = \rho_1 F_1 \tilde{h}_{1,mix} + \rho_2 F_2 \tilde{h}_{2,mix} - \rho_o F_o \tilde{h}_{o,mix} - Q \quad (2.81)$$

where $\tilde{h}_{i,mix}$ (J/kg) is the specific enthalpy of mixture i .

The specific enthalpy \tilde{h}_{mix} of n components can be written as:

$$\tilde{h}_{mix}(T, P) = \tilde{h}_{mix}(T_{ref}, P) + C_{p,mix}(T - T_{ref}) \quad (2.82)$$

where

$$\rho_{mix} \tilde{h}_{mix}(T_{ref}, P) = \sum_{i=1}^n C_i \hat{h}_i(C_i, T_{ref}, P) + C_k \Delta \hat{h}_s(C_i, T, P) \quad (2.83)$$

with \hat{h}_i (J/mole) being the molar enthalpy of component i and $\Delta \hat{h}_s$ is the heat of solution per mole of a key component k . Assume constant process pressure (P) then we can write the enthalpy of each stream as follows, taking component (A) as the key component,

$$\rho_1 \tilde{h}_{1,mix}(T_1) = C_{A1} \hat{h}_A + C_{B1} \hat{h}_B + C_{A1} \Delta \hat{h}_{1,s} + \rho_1 C_{p,1,mix}(T_1 - T_{ref}) \quad (2.84)$$

$$\rho_2 \tilde{h}_{2,mix}(T_2) = C_{A2} \hat{h}_A + C_{B2} \hat{h}_B + C_{A2} \Delta \hat{h}_{2,s} + \rho_2 C_{p,2,mix}(T_2 - T_{ref}) \quad (2.85)$$

$$\rho_o \tilde{h}_{o,mix}(T) = C_{Ao} \hat{h}_A + C_{Bo} \hat{h}_B + C_{Ao} \Delta \hat{h}_{o,s} + \rho_o C_{p,o,mix}(T - T_{ref}) \quad (2.86)$$

Substituting Eq. 2.86 into the left hand side of Eq. 2.81 and expanding yields:

$$\begin{aligned} & \frac{d(\rho_o V \tilde{h}_{o,mix})}{dt} \\ &= \hat{h}_A \frac{d(V C_{Ao})}{dt} + \hat{h}_B \frac{d(V C_{Bo})}{dt} + \Delta \hat{h}_{o,s} \frac{d(V C_{Ao})}{dt} + \rho C_p V \frac{dT}{dt} + \rho C_p T \frac{dV}{dt} \end{aligned} \quad (2.87)$$

The right hand side of equation (2.81) is equal after some manipulation to:

$$\begin{aligned}
& \hat{h}_A(C_{A1}F_1 + C_{A2}F_2 - C_{Ao}F_o) + \hat{h}_B(C_{B1}F_1 + C_{B2}F_2 - C_{Bo}F_o) \\
& + (C_{A1}F_1\Delta\hat{h}_{1,s} + C_{A2}F_2\Delta\hat{h}_{2,s} - C_{Ao}F_o\Delta\hat{h}_{o,s}) \\
& + \rho C_p(F_1T_1 + F_2T_2 - F_oT_o) - Q
\end{aligned} \tag{2.88}$$

Substituting into the right hand side of Eq. 2.87, the total mass balance equation (Eq. 2.76) and the component balance equation for species (A) (Eq. 2.77) and that of B (Eq. 2.80), and equating Eq. 2.87 to Eq. 2.88 yields, after some manipulations:

$$\begin{aligned}
\rho V C_p \frac{dT}{dt} = & C_{A1}F_1(\Delta\hat{h}_{1,s} - \Delta\hat{h}_{o,s}) + C_{A2}F_2(\Delta\hat{h}_{2,s} - \Delta\hat{h}_{o,s}) \\
& + \rho C_p(F_1(T_1 - T) + F_2(T_2 - T)) - Q
\end{aligned} \tag{2.89}$$

The mixer is then described by three ODE's Equations (2.76, 2.79, 2.89). To these relations we should add the relations that give the heats of mixing:

$$\Delta\hat{h}_{1,s} = f_1(C_{A1}, C_{B1}, T_1) \tag{2.90}$$

$$\Delta\hat{h}_{2,s} = f_2(C_{A2}, C_{B2}, T_2) \tag{2.91}$$

$$\Delta\hat{h}_{o,s} = f_3(C_{Ao}, C_{Bo}, T_o) \tag{2.92}$$

Degrees of freedom analysis

- Parameter of constant values: $\rho, A, T_{ref}, C_p, \hat{h}_A$ and \hat{h}_B
- (Forced variable): $F_1, F_2, C_{A1}, C_{A2}, T_1$ and T_2
- Remaining variables: $V, F_o, T_o, C_{Ao}, Q, \Delta\hat{h}_{1,s}, \Delta\hat{h}_{2,s}, \Delta\hat{h}_{o,s}$
- Number of equations: 6 (Eq. 2.76, 2.79, 2.89 and 2.90-2.92)

The degree of freedoms is therefore $8 - 6 = 2$. The two needed relations are the relation between effluent stream F_o and height L and the relation between the heat Q and temperature T_o in either open loop or closed-loop operations.

2.1.6 Heat Exchanger

Consider the shell and tube heat exchanger shown in figure 2.10. Liquid A of density ρ_A is flowing through the inner tube and is being heated from temperature T_{A1} to T_{A2} by liquid B of density ρ_B flowing counter-currently around the tube. Liquid B sees its temperature decreasing from T_{B1} to T_{B2} . Clearly the temperature of both liquids varies not only with time but also along the tubes (i.e. axial direction) and possibly with the radial direction too. Tubular heat exchangers are therefore typical examples of distributed parameters systems. A rigorous model would require writing a microscopic balance around a differential element of the system. This would lead to a set of partial differential equations. However, in many practical situations we would like to model the tubular heat exchanger using simple ordinary differential equations. This can be possible if we think about the heat exchanger within the unit as being an exchanger between two perfect mixed tanks. Each one of them contains a liquid.

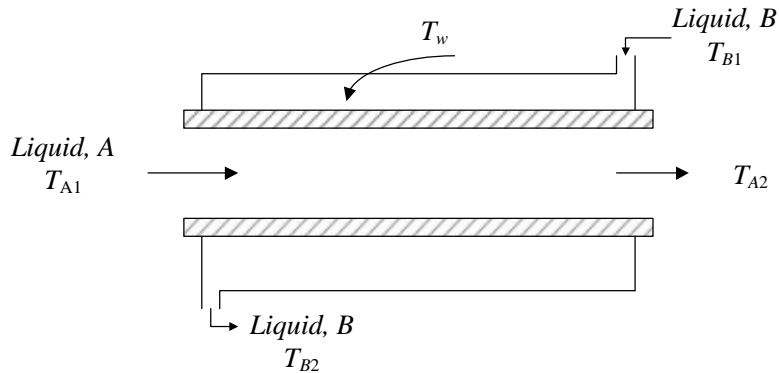


Figure 2-10 Heat Exchanger

For the time being we neglect the thermal capacity of the metal wall separating the two liquids. This means that the dynamics of the metal wall are not included in the model. We will also assume constant densities and constant average heat capacities.

One way to model the heat exchanger is to take as state variable the exit temperatures T_{A2} and T_{B2} of each liquid. A better way would be to take as state variable not the exit temperature but the average temperature between the inlet and outlet:

$$T_A = \frac{T_{A1} + T_{A2}}{2} \quad (2.93)$$

$$T_B = \frac{T_{B1} + T_{B2}}{2} \quad (2.94)$$

For liquid A, a macroscopic energy balance yields:

$$\rho_A C_{pA} V_A \frac{dT_A}{dt} = \rho_A F_A C_{pA} (T_{A1} - T_{A2}) + Q \quad (2.95)$$

where Q (J/s) is the rate of heat gained by liquid A. Similarly for liquid B:

$$\rho_B C_{pB} V_B \frac{dT_B}{dt} = \rho_B F_B C_{pB} (T_{B1} - T_{B2}) - Q \quad (2.96)$$

The amount of heat Q exchanged is:

$$Q = UA_H (T_B - T_A) \quad (2.97)$$

Or using the log mean temperature difference:

$$Q = UA_H \Delta T_{lm} \quad (2.98)$$

where

$$\Delta T_{lm} = \frac{(T_{A2} - T_{B1}) - (T_{A1} - T_{B2})}{\ln \frac{(T_{A2} - T_{B1})}{(T_{A1} - T_{B2})}} \quad (2.99)$$

with U (J/m^2s) and A_H (m^2) being respectively the overall heat transfer coefficient and heat transfer area. The heat exchanger is therefore describe by the two simple ODE's (Eq. 2.95) and (Eq. 2.96) and the algebraic equation (Eq. 2.97).

Degrees of freedom analysis

- Parameter of constant values: $\rho_A, C_{pA}, V_A, \rho_B, C_{pB}, V_B, U, A_H$
- (Forced variable): T_{A1}, T_{B1}, F_A, F_B
- Remaining variables: T_{A2}, T_{B2}, Q
- Number of equations: 3 (Eq. 2.95, 2.96, 2.97)

The degree of freedom is $5 - 3 = 2$. The two extra relations are obtained by noting that the flows F_A and F_B are generally regulated through valves to avoid fluctuations in their values.

So far we have neglected the thermal capacity of the metal wall separating the two liquids. A more elaborated model would include the energy balance on the metal wall as well. We assume that the metal wall is of volume V_w , density ρ_w and constant heat capacity C_{pw} . We also assume that the wall is at constant temperature T_w , not a bad assumption if the metal is assumed to have large conductivity and if the metal is not very thick. The heat transfer depends on the heat transfer coefficient $h_{o,t}$ on the outside and on the heat transfer coefficient $h_{i,t}$ on the inside. Writing the energy balance for liquid B yields:

$$\rho_B C_{pB} V_B \frac{dT_B}{dt} = \rho_B F_B C_{pB} (T_{B1} - T_{B2}) - h_{o,t} A_{o,t} (T_B - T_w) \quad (2.100)$$

where $A_{o,t}$ is the outside heat transfer area. The energy balance for the metal yields:

$$\rho_w C_{pw} V_w \frac{dT_w}{dt} = h_{o,t} A_{o,t} (T_B - T_w) - h_{i,t} A_{i,t} (T_w - T_A) \quad (2.101)$$

where $A_{i,t}$ is the inside heat transfer area. . The energy balance for liquid A yields:

$$\rho_A C_{p_A} V_A \frac{dT_A}{dt} = \rho_A F_A C_{p_A} (T_{A1} - T_{A2}) + h_{i,t} A_{i,t} (T_w - T_A) \quad (2.102)$$

Note that the introduction of equation (Eq. 2.101) does not change the degree of freedom of the system.

Heat Exchanger with Steam

A common case in heat exchange is when a liquid L is heated with steam (Figure 2.11). If the pressure of the steam changes then we need to write both mass and energy balance equations on the steam side.

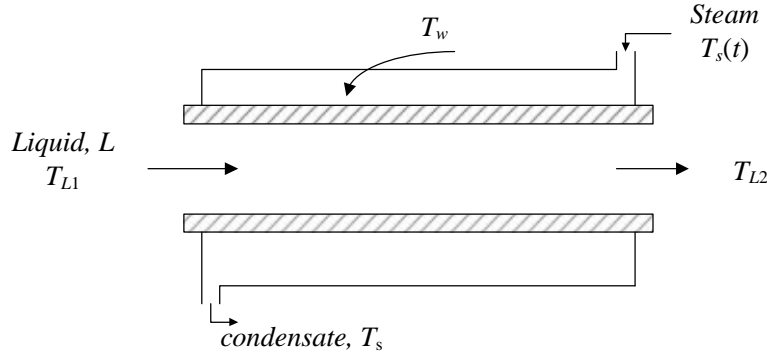


Figure 2-11 Heat Exchanger with Heating Steam

The energy balance on the tube side gives:

$$\rho_L C_{p_L} V_L \frac{dT_L}{dt} = \rho_L F_L C_{p_L} (T_{L1} - T_{L2}) + Q_s \quad (2.103)$$

where

$$T_L = \frac{T_{L1} + T_{L2}}{2} \quad (2.104)$$

$$Q_s = UA_s (T_s - T_L) \quad (2.105)$$

The steam saturated temperature T_s is also related to the pressure P_s :

$$T_s = T_s(P) \quad (2.106)$$

Assuming ideal gas law, then the mass flow of steam is:

$$m_s = \frac{M_s P_s V_s}{RT_s} \quad (2.107)$$

where M_s is the molecular weight and R is the ideal gas constant. The mass balance for the steam yields:

$$\frac{M_s V_s}{RT_s} \frac{dP}{dt} = \rho_s F_s - \rho_c F_c \quad (2.108)$$

where F_c and ρ_c are the condensate flow rate and density. The heat losses at the steam side are related to the flow of the condensate by:

$$Q_s = F_c \lambda_s \quad (2.109)$$

Where λ_s is the latent heat.

Degrees of freedom analysis

- Parameter of constant values: $\rho_L, C_{pL}, M_s, A_s, U, M_s, R$
- (Forced variable): T_{L1}
- Remaining variables: $T_{L2}, F_L, T_s, F_s, P_s, Q_s, F_c$
- Number of equations: 5 (Eq. 2.103, 2.105, 2.106, 2.108, 2.109)

The degrees of freedom is therefore $7 - 5 = 2$. The extra relations are given by the relation between the steam flow rate F_s with the pressure P_s either in open-loop or closed-loop operations. The liquid flow rate F_1 is usually regulated by a valve.

2.1.9 Single Stage Heterogeneous Systems: Multi-component flash drum

The previous treated examples have discussed processes that occur in one single phase. There are several chemical unit operations that are characterized with more than one phase. These processes are known as heterogeneous systems. In the following we cover some examples of these processes. Under suitable simplifying assumptions, each phase can be modeled individually by a macroscopic balance.

A multi-component liquid-vapor separator is shown in figure 2.12. The feed consists of N_c components with the molar fraction z_i ($i=1,2,\dots, N_c$). The feed at high temperature and pressure passes through a throttling valve where its pressure is reduced substantially. As a result, part of the liquid feed vaporizes. The two phases are assumed to be in phase equilibrium. x_i and y_i represent the mole fraction of component i in the liquid and vapor phase respectively. The formed vapor is drawn off the top of the vessel while the liquid comes off the bottom of the tank. Taking the whole tank as our system of interest, a model of the system would consist in writing separate balances for vapor and liquid phase. However since the vapor volume is generally small we could neglect the dynamics of the vapor phase and concentrate only on the liquid phase.

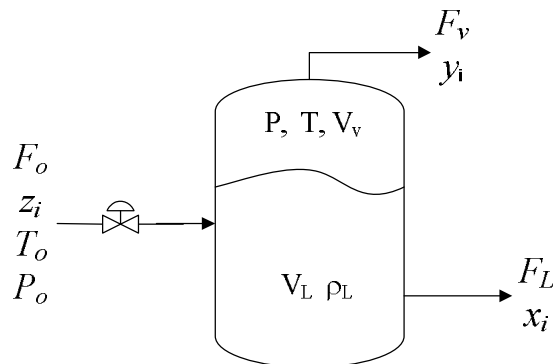


Figure 2-12 Multicomponent Flash Drum

For liquid phase:

Total mass balance:

$$\frac{d(\rho_L V_L)}{dt} = \rho_f F_f - \rho_L F_L - \rho_v F_v \quad (2.110)$$

Component balance:

$$\frac{d(\rho_L V_L x_i)}{dt} = \rho_f F_f z_i - \rho_L F_L x_i - \rho_v F_v y_i \quad (i=1,2,\dots,N_c-1) \quad (2.111)$$

Energy balance:

$$\frac{d(\rho_L V_L \tilde{h})}{dt} = \rho_f F_f \tilde{h}_f - \rho_L F_L \tilde{h} - \rho_v F_v \tilde{H} \quad (2.112)$$

where \tilde{h} and \tilde{H} are the specific enthalpies of liquid and vapor phase respectively.

In addition to the balance equations, the following supporting thermodynamic relations can be written:

- Liquid-vapor Equilibrium:

Raoult's law can be assumed for the phase equilibrium

$$y_i = \frac{x_i P_i^s}{P} \quad (i=1,2,\dots,N_c) \quad (2.113)$$

Together with the consistency relationships:

$$\sum_{i=1}^{N_c} y_i = 1 \quad (2.114)$$

$$\sum_{i=1}^{N_c} x_i = 1 \quad (2.115)$$

- Physical Properties:

The densities and enthalpies are related to the mole fractions, temperature and pressure through the following relations:

$$\rho_L = f(x_i, T, P) \quad (2.116)$$

$$\rho_v = f(y_i, T, P) \approx M_v^{\text{ave}} P / R T \quad (2.117)$$

$$M_v^{\text{ave}} = \sum_{i=1}^{N_c} y_i M_i \quad (2.118)$$

$$h = f(x_i, T) \approx \sum_{i=1}^{N_c} x_i C p_i (T - T_{\text{ref}}) \quad (2.119)$$

$$H = f(y_i, T) \approx \sum_{i=1}^{N_c} y_i C p_i (T - T_{\text{ref}}) + \lambda_m \quad (2.120)$$

$$\lambda_m = \sum_{i=1}^{N_c} y_i \lambda_i \quad (2.121)$$

Degrees of freedom analysis:

- Forcing variables: F_f, T_f, P_f, z_i ($i=1, 2, \dots, N_c$),
- Remaining variables: $2N_c+5$: V_L, F_L, F_V, P, T, x_i ($i=1, 2, \dots, N_c$), y_i ($i=1, 2, \dots, N_c$)
- Number of equations: $2N_c+3$: (Eq. 2.110, 2.111, 2.112, 2.113, 2.114, 2.115)

Note that physical properties are not included in the degrees of freedom since they are specified through given relations. The degrees of freedom is therefore $(2N_c+5)-(2N_c+3)=2$. Generally the liquid holdup (V_L) is controlled by the liquid outlet flow rate (F_L) while the pressure is controlled by F_V . In this case, the problem becomes well defined for a solution.

2-1-10 Two-phase Reactor

Consider the two phase reactor shown in figure 2.13. Gaseous A and liquid B enters the reactor at molar flow rates F_A and F_B respectively. Reactant A diffuses into the liquid phase with molar flux (N_A) where it reacts with B producing C . The latter diffuses into the vapor phase with molar flux (N_C). Reactant B is nonvolatile. The product C is withdrawn with the vapor leaving the reactor. The objective is to write the mathematical equations that describe the dynamic behavior of the process. We consider all flows to be in molar rates.

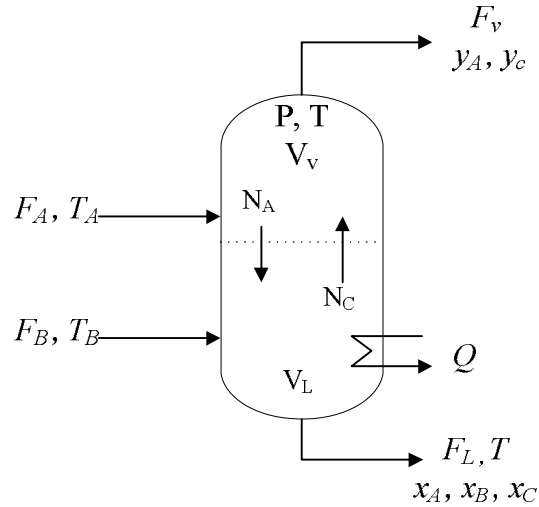


Figure 2-4 Two Phase Reactor

Assumptions:

- The individual phases are well mixed and they are in physical equilibrium at pressure P and temperature T .
- The physical properties such as molar heat capacity C_p , density ρ , and latent heat of vaporization λ are constant and equal for all the species.
- The reaction mechanism is: $A+B \rightarrow C$ and its rate has the form: $R_c = k C_A C_B V_L$
- The two phases are in equilibrium and follows the Raoult's law.
- Total enthalpy for the system is given as: $H = N_L H_L + N_v H_v$ where H_L and H_v are molar enthalpies in the liquid and vapor phases respectively, and N_L and N_v are their corresponding molar holdups.

The assumption of well mixing allows writing the following macroscopic balances:

Vapor phase:

Total mass balance:

$$\frac{dN_v}{dt} = F_A - N_A + N_c - F_v \quad (2.122)$$

Component balance for A:

$$\frac{d(N_v y_A)}{dt} = F_A - N_A - F_v y_A \quad (2.123)$$

Since $d(N_v y_A)/dt = N_v dy_A/dt + y_A dN_v/dt$, and using equation (2.122), equation (2.123) can be written as follows:

$$N_v \frac{dy_A}{dt} = F_A(1 - y_A) - N_A(1 - y_A) - N_c y_A \quad (2.124)$$

Liquid phase:

Total mass balance:

$$\frac{dN_L}{dt} = F_B + N_A - N_c - F_L - R_c \quad (2.125)$$

Component balance for A:

$$\frac{d(N_L x_A)}{dt} = N_A - F_L x_A - R_c \quad (2.126)$$

Since $d(N_L x_A)/dt = N_L dx_A/dt + x_A dN_L/dt$, and using equation (2.125), equation (2.126) can be written as follows:

$$N_L \frac{dx_A}{dt} = N_A(1 - x_A) - F_B x_A - R_c(1 - x_A) + N_c x_A \quad (2.127)$$

Component balance for B:

Repeating the same reasoning used for component A, we can write:

$$N_L \frac{dx_B}{dt} = N_A(1 - x_B) + F_B x_B - R_c(1 - x_B) + N_c x_B \quad (2.128)$$

Energy balance, assuming $T_{\text{ref}} = 0$:

$$\frac{d(N_L H_L + N_v H_v)}{dt} = F_B C_p T_B + F_A (C_p T_A + \lambda) - F_L C_p T - F_v C_p T - R_c \Delta H_r + Q \quad (2.129)$$

Note that:

$$\frac{d(N_L H_L)}{dt} = N_L \frac{d(H_L)}{dt} + H_L \frac{d(N_L)}{dt} = N_L C_p \frac{d(T)}{dt} + C_p T \frac{d(N_L)}{dt} \quad (2.130)$$

$$\frac{d(N_v H_v)}{dt} = N_v \frac{d(H_v)}{dt} + H_v \frac{d(N_v)}{dt} = N_v C_p \frac{d(T)}{dt} + (C_p T + \lambda) \frac{d(N_v)}{dt} \quad (2.131)$$

Substituting the last two equations, and using the definition of dN_L/dt and dN_v/dt from equations (2.122) and (2.125), in equation (2.131) yields:

$$N_L + N_v \frac{d(T)}{dt} = F_A (T_A - T) + F_B (T_B - T) + R_c (T - \frac{\Delta H_r}{C_p}) + \frac{\lambda}{C_p} (N_A - N_c) + \frac{Q}{C_p} \quad (2.132)$$

The following additional equations are needed:

Vapor-liquid equilibrium relations:

$$y_A P - x_A P_A^s = 0 \quad (2.133)$$

$$y_A P - (1 - x_A - x_B) P_c^s = 0 \quad (2.134)$$

Total volume constraint:

$$V = V_L + V_v \quad (2.135)$$

Or, using ideal gas law for vapor volume and total volume and knowing that $V_L = N_L/\rho$, we can write:

$$nRT = N_v RT + N_L P/\rho \quad (2.136)$$

or

$$V = N_v RT/P + N_L/\rho \quad (2.137)$$

Degrees of freedom analysis:

- Forcing variables: F_A, F_B, T_A, T_B, Q, P
- Physical properties and parameters: $\Delta H_r, Cp, \lambda, R, \rho, V, P_A^s, P_C^s$
- Remaining variables: $N_A, N_C, N_L, N_v, F_L, T, x_A, x_B, y_A$
- Number of equations: (Eq. 2.122, 2.124, 2.125, 2.127, 2.128, 2.132, 2.133, 2.134, 2.137)

The degree of freedom is $9-9=0$ and the problem is exactly specified. Note that the reaction rate R_c is defined and that the outlet flow F_v can be determined from the overall mass balance.

2-1-11 Reaction with Mass Transfer

Figure 2.14 shows a chemical reaction that takes place in a gas-liquid environment. The reactant A enters the reactor as a gas and the reactant B enters as a liquid. The gas dissolves in the liquid where it chemically reacts to produce a liquid C . The product is drawn off the reactor with the effluent F_L . The un-reacted gas vents off the top of the vessel. The reaction mechanism is given as follows:



Assumptions:

- Perfectly mixed reactor
- Isothermal operation
- Constant pressure, density, and holdup.

- Negligible vapor holdup.

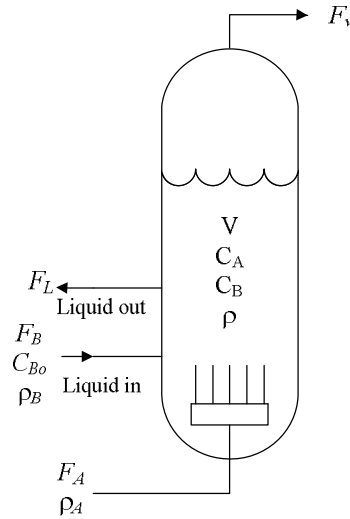


Figure 2-14 Reaction with Mass Transfer

In such cases, when the two chemical phenomena, i.e., mass transfer and chemical reaction, occur together, the reaction process may become mass transfer dominant or reaction-rate dominant. If the mass transfer is slower reaction rate, then mass transfer prevail and vise versa.

Due to the perfectly mixing assumption, macroscopic mass transfer of component A from the bulk gas to the bulk liquid is approximated by the following molar flux:

$$N_A = K_L (C_A^* - C_A) \quad (2.139)$$

where

- | | |
|---------|--|
| K_L | is mass transfer coefficient |
| C_A^* | is gas concentration at gas-liquid interface |
| C_A | is gas concentration in bulk liquid |

To fully describe the process, we derive the macroscopic balance of the liquid phase where the chemical reaction takes place. This results in:

Liquid phase:

Total mass balance:

$$\frac{d\rho V}{dt} = \rho_B F_B + M_A A_m N_A - \rho F_L \quad (2.140)$$

Component balance on A:

$$V \frac{dC_A}{dt} = A_m N_A - F_L C_A - rV \quad (2.141)$$

Component balance on B:

$$V \frac{dC_B}{dt} = F_B C_{B0} - F_L C_B - rV \quad (2.142)$$

Vapor phase:

Here, since vapor holdup is negligible, we can write a steady state total continuity equation as follows:

$$F_v = F_A - M_A A_m N_A / \rho_A \quad (2.143)$$

where

- A_m total mass transfer area of the gas bubble
- M_A molecular weight of component A
- ρ density
- V liquid volume

Degrees of freedom analysis:

- Forcing variables: F_A, F_B, C_{B0} ,
- Parameters of constant values: $K_L, M_A, A_m, \rho, \rho_A, \rho_B$,

- Remaining variables: C_B, N_A, C_A, F_v, V
- Number of equations: (Eq. 2.139-2.143)

Note that the liquid flow rate, F_L can be determined from the overall mass balance and that the reaction rate r should be defined.

2.1.12 Multistage Heterogeneous Systems: Liquid-liquid extraction

There are many chemical processes which consist in a number of consecutive stages in series. In each stage two streams are brought in contact for separating materials due to mass transfer. The two streams could be flow in co-current or counter current patterns. Counter-current flow pattern is known to have higher separation performance. Examples of these processes are distillation columns, absorption towers, extraction towers and multi-stage flash evaporator where distillate water is produced from brine by evaporation.

The same modeling approach used for single stage processes will be used for the staged processes, where the conservation law will be written for one stage and then repeated for the next stage and so on. This procedure will result in large number of state equation depending on the number of stages and number of components.

The separation process generally takes place in plate, packed or spray-type towers. In tray or spray-type columns the contact and the transfer between phases occur at the plates. Generally, we can always assume good mixing of phases at the plates, and therefore macroscopic balances can be carried out to model these type of towers. Packed towers on the other hand are used for continuous contacting of the two phases along the packing. The concentrations of the species in the phases vary obviously along the tower. Packed towers are therefore typical examples of distributed parameters systems that need to be modeled by microscopic balances.

In the following we present some examples of mass separation units that can be modeled by simple ODE's, and we start with liquid-liquid extraction process.

Liquid-liquid extraction is used to move a solute from one liquid phase to another. Consider the single stage countercurrent extractor, shown in Figure 2.15, where it is desired to separate a solute (A) from a mixture (W) using a solvent (S). The stream mixture with flow rate W (kg/s) enters the stage containing X_{Af} weight fraction of solute (A). The solvent with a flow rate S (kg/s) enters the stage containing Y_{Af} weight fraction of species (A). As the solvent flows through the stage it retains more of (A) thus extracting (A) from the stream (W). Our objective is to model the variations of the concentration of the solute. A number of simplifying assumptions can be used:

- The solvent is immiscible in the other phase.
- The concentration X_A and Y_A are so small that they do not affect the mass flow rates. Therefore, we can assume that the flow rates W and S are constant. A total mass balance is therefore not needed.
- An equilibrium relationship exists between the weight fraction Y_A of the solute in the solvent (S) and its weight fraction X_A in the mixture (W). The relationship can be of the form:

$$Y_A = K X_A \quad (2.144)$$

Here K is assumed constant. Since both phases are assumed perfectly mixed a macroscopic balance can be carried out on the solute in each phase. A component balance on the solute in the solvent-free phase of volume V_1 and density ρ_1 gives:

$$\rho_1 V_1 \frac{dX_A}{dt} = W X_{Af} - W X_A - N_A \quad (2.145)$$

whereas N_A (kg/s) is the flow rate due to transfer flow between the two phases. A similar component balance on the solvent phase of volume V_2 and density ρ_2 gives:

$$\rho_2 V_2 \frac{dY_A}{dt} = S Y_{Af} - S Y_A + N_A \quad (2.146)$$

Since $Y_A = K X_A$ and K is constant, the last equation is equivalent to:

$$\rho_2 V_2 K \frac{dX_A}{dt} = SY_{Af} - SKX_A + N_A \quad (2.147)$$

Adding Eq. 2.145 and 2.147 yields:

$$(\rho_1 V_1 + \rho_2 V_2 K) \frac{dX_A}{dt} = WX_{Af} + SY_{Af} - (W + KS)X_A \quad (2.148)$$

The latter is a simple linear ODE with unknown X_A . With the volume V_1 , V_2 and flow rates W , S known the system is exactly specified and it can be solved if the initial concentration is known:

$$X_A(t_i) = X_{Ai} \quad (2.149)$$

Note that we did not have to express explicitly the transferred flux N_A .

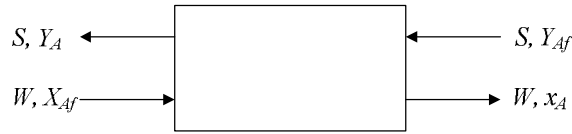


Figure 2-15 Single Stage Liquid-Liquid Extraction Unit

The same analysis can be extended to the multistage liquid/liquid extraction units as shown in Figure 2.16. The assumptions of the previous example are kept and we also assume that all the units are identical, i.e. have the same volume. They are also assumed to operate at the same temperature.

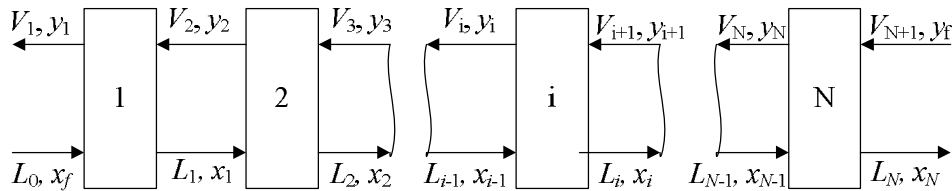


Figure 2-16 Multi-Stage Liquid-Liquid Extraction Unit

A component balance in the i^{th} stage (excluding the first and last stage) gives:

- Solvent-free phase, of volume V_{1i} and density ρ_{1i}

$$\rho_{1i} V_{1i} \frac{dX_{Ai}}{dt} = WX_{Ai-1} - WX_{Ai} - N_{Ai} \quad (i=2, \dots, N-1) \quad (2.150)$$

where N_{Ai} is the flow rate due to transfer between the two phases at stage i .

- Solvent phase of volume V_{2i} and density ρ_{2i} :

$$\rho_{2i} V_{2i} \frac{dY_{Ai}}{dt} = SY_{Ai+1} - SY_{Ai} + N_{Ai} \quad \dots \quad (i = 2, \dots, N-1) \quad (2.151)$$

Writing the equilibrium equation (Eq. 2.144) for each component $Y_{Ai} = K X_{Ai}$ ($i=1, \dots, N$) and adding the last two equations yield:

$$(\rho_{1i} V_{1i} + \rho_{2i} V_{2i} K) \frac{dX_{Ai}}{dt} = WX_{Ai-1} + SY_{Ai+1} - (W + KS) X_{Ai} \quad (i=2, \dots, N-1) \quad (2.152)$$

Since the volume and densities are equal, i.e.:

$$V_{1i} = V_1 \text{ and } V_{2i} = V \quad (2.153)$$

$$\rho_{1i} = \rho_1 \text{ and } \rho_{2i} = \rho_2 \quad (2.154)$$

Equation 2.152 is therefore equivalent to:

$$(\rho_1 V_1 + \rho_2 V_2 K) \frac{dX_{Ai}}{dt} = WX_{Ai-1} + SY_{Ai+1} - (W + KS) X_{Ai} \quad (i=2, \dots, N-1) \quad (2.155)$$

The component balance in the first stage is:

$$(\rho_1 V_1 + \rho_2 V_2 K) \frac{dX_{A1}}{dt} = W X_{Af} + S Y_{A1} - (W + KS) X_{A1} \quad (2.156)$$

And that for the last stage is:

$$(\rho_1 V_1 + \rho_2 V_2 K) \frac{dX_{AN}}{dt} = W X_{AN-1} + S Y_{Af} - (W + KS) X_{AN} \quad (2.157)$$

The model is thus formed by a system of linear ODE's (Eq. 2.155, 2.156, 2.157) which can be integrated if the initial conditions are known:

$$X_A(t_i) = X_{Ai} \quad (i=1,2,\dots,N) \quad (2.158)$$

Degrees of freedom analysis

- Parameter of constant values: ρ_1 , ρ_2 , K , V_1 , V_2 , W and S
- (Forced variable): X_{Af} , Y_{Af}
- Remaining variables: X_{Ai} (2N variables): ($i=1,2,\dots,N$) and Y_{Ai} ($i=1,2,\dots,N$)
- Number of equations: 2N [2.144 (N equations, one for each component), Eq. 2.155 (N-2 eqs), 2.156(1 eq), 2.157(1 eq)].

The problem is therefore is exactly specified.

2-1-3 Binary Absorption Column

Consider a N stages binary absorption tower as shown in figure 2.17. A Liquid stream flows downward with molar flow rate (L) and feed composition (x_f). A Vapor stream flows upward with molar flow rate (G) and feed composition (y_f). We are interested in deriving an unsteady state model for the absorber. A simple vapor-liquid equilibrium relation of the form of:

$$y_i = a x_i + b \quad (2.159)$$

can be used for each stage i ($i=1,2,\dots,N$).

Assumptions:

- Isothermal Operation
- Negligible vapor holdup
- Constant liquid holdup in each stage
- Perfect mixing in each stage

According to the second and third assumptions, the molar rates can be considered constants, i.e. not changing from one stage to another, thus, total mass balance need not be written. The last assumption allows us writing a macroscopic balance on each stage as follows:

Component balance on stage i :

$$H \frac{dx_i}{dt} = G(y_{i-1} - y_i) + L(x_{i+1} - x_i) \quad (i=2\dots,N-1) \quad (2.160)$$

where H is the liquid holdup, i.e., the mass of liquid in each stage. The last equation is repeated for each stage with the following exceptions for the last and the first stages:

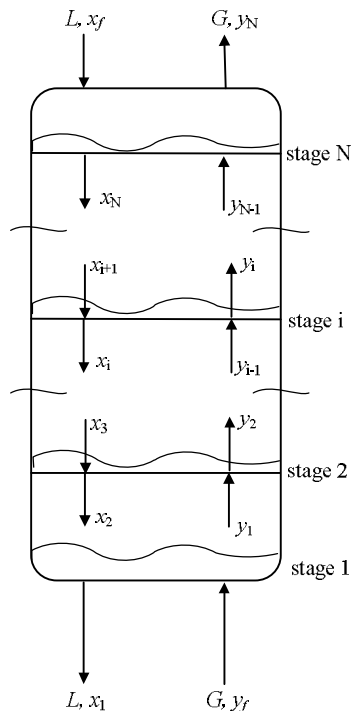


Figure 2-17 N-stages Absorption Tower

In the last stage, x_{i+1} is replaced by x_f

In the first stage, y_{i-1} is replaced by y_f

Degrees of freedom analysis

- Parameter of constant values: H, a, b
- (Forced variable): G, L, x_f, y_f
- Remaining variables: x_i ($i=1,2,\dots,N$), y_i ($i=1,2,\dots,N$)
- Number of equations: $2N$ (Eqs. 2.159, 2.160)

The problem is therefore exactly specified.

2-14 Multi-component Distillation Column

Distillation columns are important units in petrochemical industries. These units process their feed, which is a mixture of many components, into two valuable fractions namely the top product which is rich in the light components and bottom product which is rich in the heavier components. A typical distillation column is shown in Figure 2.18. The column consists of n trays excluding the re-boiler and the total condenser. The convention is to number the stages from the bottom upward starting with the re-boiler as the 0 stage and the condenser as the $n+1$ stage.

Description of the process:

The feed containing nc components is fed at specific location known as the feed tray (labeled f) where it mixes with the vapor and liquid in that tray. The vapor produced from the re-boiler flows upward. While flowing up, the vapor gains more fraction of the light component and loses fraction of the heavy components. The vapor leaves the column at the top where it condenses and is split into the product (distillate) and reflux which is returned into the column as liquid. The liquid flows down gaining more fraction of the heavy component and loses fraction of the light components. The liquid leaves the column at the bottom where it is evaporated in the re-boiler. Part of the liquid is drawn as bottom product and the rest is recycled to the column. The loss and gain of materials occur at each stage where the two phases are brought into intimate phase equilibrium.

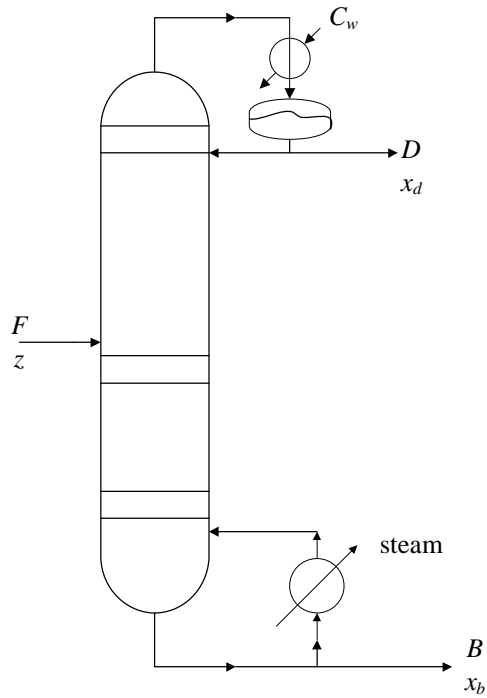


Figure 2-18 Distillation Column

Modeling the unit:

We are interested in developing the unsteady state model for the unit using the following assumptions:

- 100% tray efficiency
- Well mixed condenser drum and re-boiler.
- Liquids are well mixed in each tray.
- Negligible vapor holdups.
- liquid-vapor thermal equilibrium

Since the vapor-phase has negligible holdups, then conservation laws will only be written for the liquid phase as follows:

Stage $n+1$ (Condenser), Figure 2.19a:

Total mass balance:

$$\frac{dM_D}{dt} = V_n - (R + D) \quad (2.161)$$

Component balance:

$$\frac{d(M_D x_{D,j})}{dt} = V_n y_{n,j} - (R + D) x_{D,j} \quad j = 1, nc - 1 \quad (2.162)$$

Energy balance:

$$\frac{d(M_D h_D)}{dt} = V_n h_n - (R + D) h_D - Q_c \quad (2.163)$$

Note that $R = L_{n+1}$ and the subscript D denotes $n+1$

Stage n , Figure fig2.19b

Total Mass balance:

$$\frac{dM_n}{dt} = V_{n-1} - V_n + R - L_n \quad (2.164)$$

Component balance:

$$\frac{d(M_n x_{n,j})}{dt} = V_{n-1} y_{n-1,j} - V_n y_{n,j} + R x_{D,j} - L_n x_{n,j} \quad j = 1, nc - 1 \quad (2.165)$$

Energy balance:

$$\frac{d(M_n h_n)}{dt} = V_{n-1} H_{n-1} - V_n H_n + R h_D - L_n h_n \quad (2.166)$$

Stage i , Figure 2.19c

Total Mass balance:

$$\frac{dM_i}{dt} = V_{i-1} - V_i + L_{i+1} - L_i \quad (2.167)$$

Component balance:

$$\frac{d(M_i x_{i,j})}{dt} = V_{i-1} y_{i-1,j} - V_i y_{i,j} + L_{i+1} x_{i+1,j} - L_i x_{i,j} \quad j = 1, nc - 1 \quad (2.168)$$

Energy balance:

$$\frac{d(M_i h_i)}{dt} = V_{i-1} H_{i-1} - V_i H_i + L_{i+1} h_{i+1} - L_i h_i \quad (2.169)$$

Stage f (Feed stage), Figure 2.19d

Total Mass balance:

$$\frac{dM_f}{dt} = V_{f-1} - (V_f + (1-q)F) + L_{f+1} - (L_f + qF) \quad (2.170)$$

Component balance:

$$\frac{d(M_f x_{f,j})}{dt} = V_{f-1} y_{f-1,j} - (V_f y_{f,j} + (1-q)F z_j) + L_{f+1} x_{f+1,j} - (L_f x_{f,j} + qF z_j) \quad j = 1, nc - 1 \quad (2.171)$$

Energy balance:

$$\frac{d(M_f h_f)}{dt} = V_{f-1} H_{f-1} - (V_f H_f + (1-q)F h_f) + L_{f+1} h_{f+1} - (L_f h_f + qF h_f) \quad (2.172)$$

Stage 1, Figure 2.19e

Total Mass balance:

$$\frac{dM_1}{dt} = V_B - V_1 + L_2 - L_1 \quad (2.173)$$

Component balance:

$$\frac{d(M_1 x_{1,j})}{dt} = V_B y_{B,j} - V_1 y_{1,j} + L_2 x_{2,j} - L_1 x_{1,j} \quad j = 1, nc - 1 \quad (2.174)$$

Energy balance:

$$\frac{d(M_1 h_1)}{dt} = V_B H_B - V_1 H_1 + L_2 h_2 - L_1 h_1 \quad (2.175)$$

Stage 0 (Re-boiler), Figure 2.19f

Total Mass balance:

$$\frac{dM_B}{dt} = -V_B + L_1 - B \quad (2.176)$$

Component balance:

$$\frac{d(M_B x_{B,j})}{dt} = -V_B y_{B,j} + L_1 x_{1,j} - B x_{B,j} \quad j = 1, nc - 1 \quad (2.177)$$

Energy balance:

$$\frac{d(M_B h_B)}{dt} = -V_B H_B + L_1 h_1 - B h_B + Q_r \quad (2.178)$$

Note that $L_0 = B$ and B denotes the subscript 0

Additional given relations:

Phase equilibrium: $y_j = f(x_j, T, P)$

Liquid holdup: $M_i = f(L_i)$

Enthalpies: $H_i = f(T_i, y_{i,j})$, $h_i = f(T_i, x_{i,j})$

Vapor rates: $V_i = f(P)$

Notation:

L_i, V_i	Liquid and vapor molar rates
H_i, h_i	Vapor and liquid specific enthalpies
x_i, y_i	Liquid and vapor molar fractions
M_i	Liquid holdup
Q	Liquid fraction of the feed
Z	Molar fractions of the feed
F	Feed molar rate

Degrees of freedom analysis

Variables

M_i	n
M_B, M_D	2
L_i	n
B, R, D	3
$x_{i,j}$	$n(nc - 1)$
$x_{B,j}, x_{D,j}$	$2(nc - 1)$
$y_{i,j}$	$n(nc - 1)$
$y_{B,j}$	$nc - 1$
h_i	n
h_B, h_D	2
H_i	n
H_B	1
V_i	n
V_B	1
T_i	n
T_D, T_B	2
<hr/> <i>Total</i>	<hr/> $11+6n+2n(nc-1)+3(nc-1)$

Equations:

Total Mass	$n + 2$
Energy	$n + 2$
Component	$(n + 2)(nc - 1)$
Equilibrium	$n(nc - 1)$
Liquid holdup	n
Enthalpies	$2n+2$
Vapor rate	n
$h_B = h_1$	1
$y_B = x_B$	$(nc - 1)$
<hr/>	
Total	$7+6n+2n(nc-1)+3(nc-1)$

Constants: P, F, Z

Therefore; the degree of freedom is 4

To well define the model for solution we include four relations imported from inclusion of four feedback control loops as follows:

- Use B , and D to control the liquid level in the condenser drum and in the re-boiler.
- Use V_B and R to control the end compositions i.e., x_B, x_D

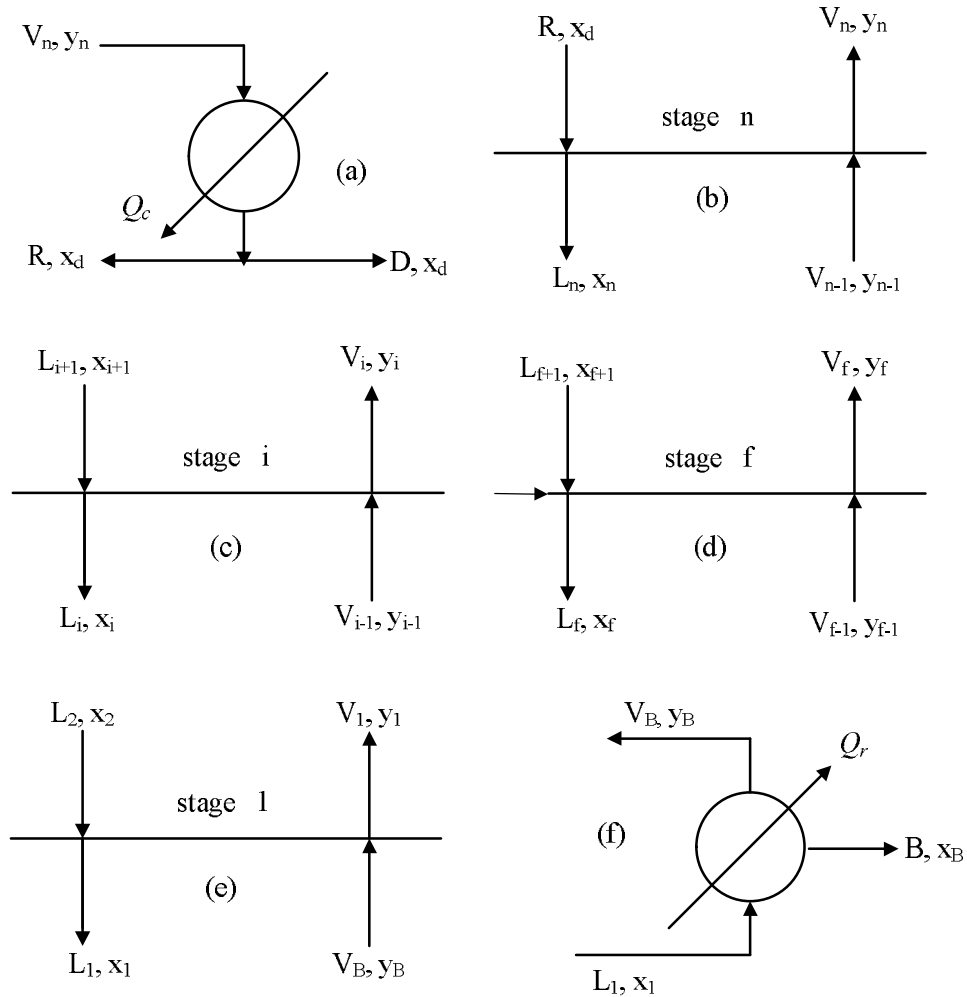


Figure 2-19 Distillation Column Stages

Simplified Model

One can further simplify the foregoing model by the following assumptions:

- (a) Equi-molar flow rates, i.e. whenever one mole of liquid vaporizes a tantamount of vapor condenses. This occur when the molar heat of vaporization of all components are about the same. This assumption leads to further idealization that implies constant temperature over the entire column, thus neglecting the energy balance. In addition, the vapor rate through the column is constant and equal to:

$$V_B = V_1 = V_2 = \dots = V_n \quad (2.179)$$

(b) Constant relative volatility, thus a simpler formula for the phase equilibrium can be used:

$$y_j = \alpha_j x_j / (1 + (\alpha_j - 1) x_j) \quad (2.180)$$

Degrees of Freedom:

Variables:

M_i, M_B, M_D	$n + 2$
L_i, B, R, D	$n + 3$
x_i, x_B, x_D	$(n + 2)(nc - 1)$
y_j, y_B	$(n + 1)(nc - 1)$
V	1
<i>Total</i>	$2 + 2n + (2n + 3)(nc - 1)$

Equations:

Total Mass	$n + 2$
Component	$(n + 2)(nc - 1)$
Equilibrium	$n(nc - 1)$
Liquid holdup	n
$y_B = x_B$	1
<hr/>	
Total	$2 + 2n + (2n + 3)(nc - 1)$

It is obvious that the degrees of freedom is still 4.

2.2 Examples of Distributed Parameter Systems

2.2.1 Liquid Flow in a Pipe

Consider a fluid flowing inside a pipe of constant cross sectional area (A) as shown in Figure 2.20. We would like to develop a mathematical model for the change in the fluid mass inside the pipe. Let v be the velocity of the fluid. Clearly the velocity changes with time (t), along the pipe length (z) and also with the radial direction (r). In order to simplify the problem, we assume that there are no changes in the radial direction. We also assume isothermal conditions, so only the mass balance is needed. Since the velocity changes with both time and space, the mass balance is to be carried out on microscopic scale. We consider therefore a shell element of width Δz and constant cross section area (A) as shown in Fig. 2.20.

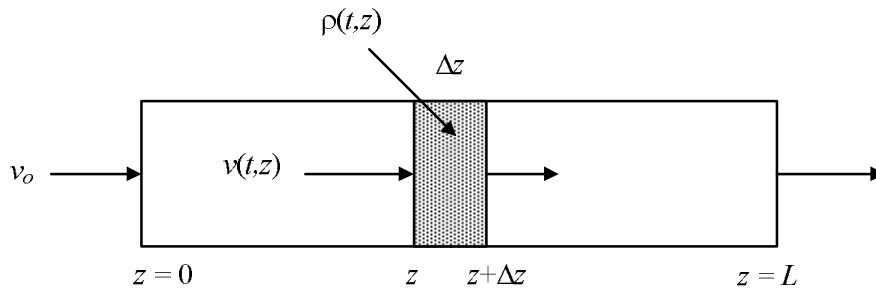


Figure 2-20 Liquid flow in a pipe

Mass into the shell:

$$\rho v A \Delta t|_z \quad (2.181)$$

where the subscript $(\cdot|_z)$ indicates that the quantity (\cdot) is evaluated at the distance z .

Mass out of the shell:

$$\rho v A \Delta t|_{z+\Delta z} \quad (2.182)$$

Accumulation:

$$\rho A \Delta z|_{t+\Delta t} - \rho A \Delta z|_t \quad (2.183)$$

Similarly the subscript $(\cdot)_t$ indicates that the quantity (\cdot) is evaluated at the time t .

The mass balance equation is therefore:

$$\rho v A \Delta t|_z = \rho v A \Delta t|_{z+\Delta z} + \rho A \Delta z|_{t+\Delta t} - \rho A \Delta z|_t \quad (2.184)$$

We can check for consistency that the units in each term are in (kg) . Dividing Eq. 2.184 by $\Delta t \Delta z$ and rearranging yields:

$$\frac{(\rho A)|_{t+\Delta t} - (\rho A)|_t}{\Delta t} = -\frac{(\rho v A)|_z - (\rho v A)|_{z+\Delta z}}{\Delta z} \quad (2.185)$$

Taking the limit as $\Delta t \rightarrow 0$ and $\Delta z \rightarrow 0$ gives:

$$\frac{\partial(\rho A)}{\partial t} = -\frac{\partial(\rho v A)}{\partial z} \quad (2.186)$$

Since the cross section area (A) is constant, Eq. 2.186 yields:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial(\rho v)}{\partial z} \quad (2.187)$$

or

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v)}{\partial z} = 0 \quad (2.188)$$

The ensuing equation is a partial differential equation (PDE) that defines the variation of ρ and v with the two independent variables t and z . This equation is known as the one-dimensional continuity equation. For incompressible fluids for which the density is constant, the last equation can also be written as:

$$\frac{\partial v}{\partial z} = 0 \quad (2.189)$$

This indicates that the velocity is independent of axial direction for one dimensional incompressible flow.

2.2.2 Velocity profile inside a pipe

We reconsider the flow inside the pipe of the previous example. Our objective is to find the velocity profile in the pipe at steady state. For this purpose a momentum balance is needed. To simplify the problem we also assume that the fluid is incompressible. We will carry out a microscopic momentum balance on a shell with radius r , thickness Δr and length Δz as shown in Fig 2.21.

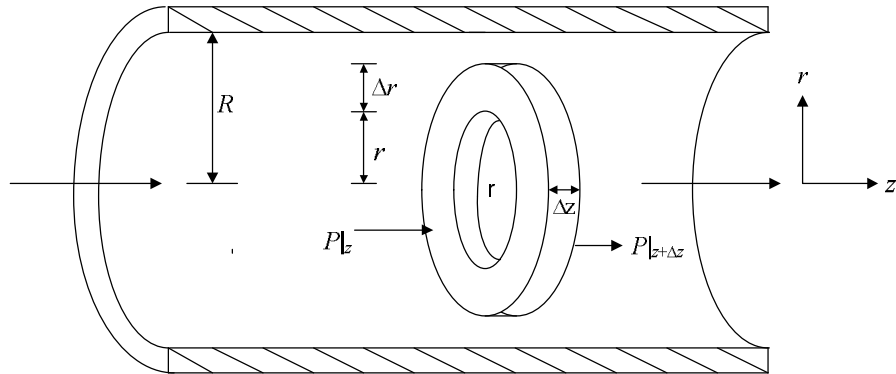


Figure 2-21 Velocity profile for a laminar flow in a pipe

Momentum in:

$$(\tau_{rz} 2\pi r \Delta z)|_r \quad (2.190)$$

where τ_{rz} is the shear stress acting in the z -direction and perpendicular to the radius r .

Momentum out:

$$(\tau_{rz}2\pi r\Delta z)|_{r+\Delta r} \quad (2.191)$$

As for the momentum generation we have mentioned earlier in section 1.8.3 that the generation term corresponds to the sum of forces acting on the volume which in this example are the pressure forces, i.e.

$$(PA)|_z - (PA)|_{z+\Delta z} = P(2\pi r\Delta r)|_z - P(2\pi r\Delta r)|_{z+\Delta z} \quad (2.192)$$

There is no accumulation term since the system is assumed at steady state. Substituting this term in the balance equation (Eq. 1.6) and rearranging yields,

$$\frac{r\tau_{rz}|_{r+\Delta r} - r\tau_{rz}|_r}{\Delta r} = \frac{r(P|_z - P|_{z+\Delta z})}{\Delta z} \quad (2.193)$$

We can check for consistency that all the terms in this equation have the SI unit of (N/m^2) . Taking the limit of (Eq. 2.193) as Δz and Δr go to zero yields:

$$\frac{d(r\tau_{rz})}{dr} = -r \frac{dP}{dz} \quad (2.194)$$

Here we will make the assumption that the flow is fully developed, i.e. it is not influenced by the entrance effects. In this case the term dP/dz is constant and we have:

$$\frac{dP}{dz} = \frac{P_2 - P_1}{L} = \frac{\Delta P}{L} \quad (2.195)$$

where L is the length of the tube. Note that equation (2.195) is a function of the shear stress τ_{rz} , but shear stress is a function of velocity. We make here the assumption that the fluid is Newtonian, that is the shear stress is proportional to the velocity gradient:

$$\tau_{rz} = -\mu \frac{dv_z}{dr} \quad (2.196)$$

Substituting this relation in Eq. 2.194 yields:

$$\mu \frac{d}{dr} \left(\frac{r dv_z}{dr} \right) = r \frac{\Delta P}{L} \quad (2.197)$$

or by expanding the derivative:

$$\mu \left(\frac{d^2 v_z}{dr^2} + \frac{1}{r} \frac{dv_z}{dr} \right) = \frac{\Delta P}{L} \quad (2.198)$$

The system is described by the second order ODE (Eq. 2.198). This ODE can be integrated with the following conditions:

- The velocity is zero at the wall of the tube

$$v_z = 0 \quad \text{at } r = R \quad (2.199)$$

- Due to symmetry, the velocity profile reaches a maximum at the center of the tube:

$$\frac{dv_z}{dr} = 0 \quad \text{at } r = 0 \quad (2.200)$$

Note that the one-dimensional distributed parameter system has been reduced to a lumped parameter system at steady state.

2.2.3 Diffusion with chemical reaction in a slab catalyst

We consider the diffusion of a component A coupled with the following chemical reaction $A \rightarrow B$ in a slab of catalyst shown in figure 2.22. Our objective is to determine the variation of the concentration at steady state. The concentration inside the

slab varies with both the position z and time t . The differential element is a shell element of thickness Δz .

Flow of moles A in:

$$(SN_A)|_z \quad (2.201)$$

where S (m^2) is the surface area and N_A (*moles A/s m²*) is the molar flux.

Flow of moles A out:

$$(SN_A)|_{z+\Delta z} \quad (2.202)$$

Rate of generation of A :

$$-(S\Delta z)r \quad (2.203)$$

where $r = kC_A$ is the rate of reaction, assumed to be of first order. There is no accumulation term since the system is assumed at steady state. The mass balance equation is therefore,

$$(SN_A)|_z - (SN_A)|_{z+\Delta z} - (S\Delta z)kC_A = 0 \quad (2.204)$$

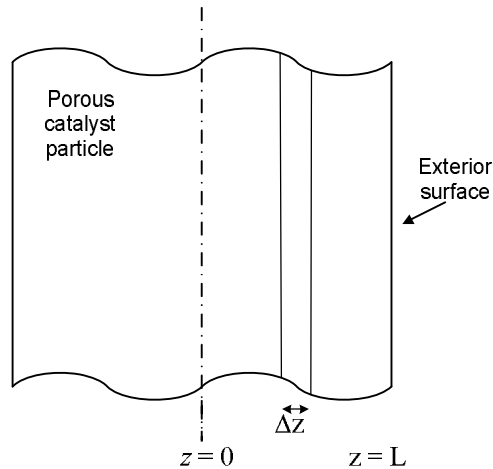


Figure 2-22 diffusion with chemical reaction inside a slab catalyst

Dividing equation (2.204) by $S\Delta z$ results in:

$$\frac{(N_A)|_z - (N_A)|_{z+\Delta z}}{\Delta z} - kC_A = 0 \quad (2.205)$$

Taking the limit when $\Delta z \rightarrow 0$, the last equation becomes:

$$\frac{dN_A}{dz} - kC_A = 0 \quad (2.206)$$

The molar flux is given by Fick's law as follows:

$$N_A = -D_A \frac{dC_A}{dz} \quad (2.207)$$

where D_A is diffusivity coefficient of (A) inside the catalyst particle. Equation (2.206) can be then written as follows:

$$D_A \frac{d^2 C_A}{dz^2} - kC_A = 0 \quad (2.208)$$

This is also another example where a one-dimensional distributed system is reduced to a lumped parameter system at steady state. In order to solve this second-order ODE, the following boundary conditions could be used:

$$\text{at } z = L, C_A = C_{Ao} \quad (2.209)$$

$$\text{at } z = 0, dC_A/dr = 0 \quad (2.210)$$

The first condition imposes the bulk flow concentration C_{Ao} at the end length of the slab. The second condition implies that the concentration is finite at the center of the slab.

2.2.4 Temperature profile in a heated cylindrical Rod

Consider a cylindrical metallic rod of radius R and length L , initially at a uniform temperature of T_o . Suppose that one end of the rod is brought to contact with a hot fluid of temperature T_m while the surface area of the rod is exposed to ambient temperature of T_a . We are interested in developing the mathematical equation that describes the variation of the rod temperature with the position. The metal has high thermal conductivity that makes the heat transfer by conduction significant. In addition, the rod diameter is assumed to be large enough such that thermal distribution in radial direction is not to be neglected. The system is depicted by figure 2.23. For modeling we take an annular ring of width Δz and radius Δr as shown in the figure. The following transport equation can be written:

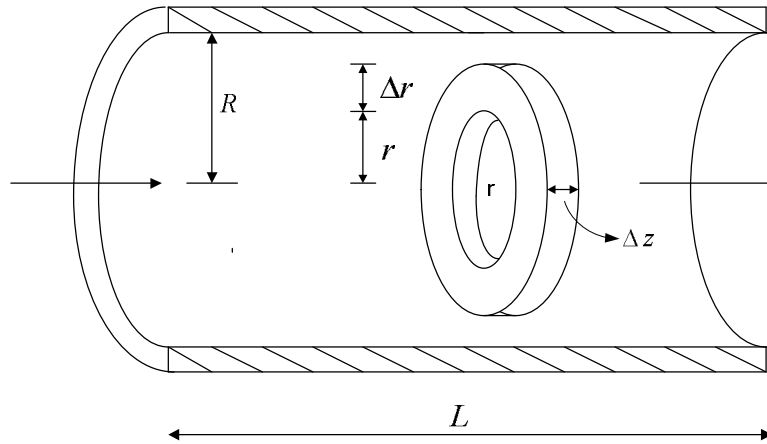


Figure 2-23 Temperature Distribution In a cylindrical rod

Heat flow in by conduction at z :

$$q_z(2\pi r \Delta r)\Delta t \quad (2.211)$$

Heat flow in by conduction at r :

$$q_r(2\pi r \Delta z)\Delta t \quad (2.212)$$

where q_z and q_r are the heat flux by conduction in the z and r directions.

Heat flow out by conduction at $z+\Delta z$:

$$q_{z+\Delta z}(2\pi r \Delta r)\Delta t \quad (2.213)$$

Heat flow out by conduction at $r+\Delta r$:

$$q_{r+\Delta r}(2\pi (r+\Delta r)\Delta z)\Delta t \quad (2.214)$$

Heat accumulation:

$$\rho(2\pi r \Delta r \Delta z)(\tilde{h}_{t+\Delta t} - \tilde{h}_t) \quad (2.215)$$

where \tilde{h} is the specific enthalpy. Summing the above equation according to the conservation law and dividing by $(2\pi \Delta r \Delta z \Delta t)$, considering constant density, gives:

$$\rho r \frac{\tilde{h}_{t+\Delta t} - \tilde{h}_t}{\Delta t} = r \frac{q_z - q_{z+\Delta z}}{\Delta z} + \frac{r q_r - r q_{r+\Delta r}}{\Delta r} \quad (2.216)$$

Taking the limit of Δt , Δz , and Δr go to zero yield:

$$\rho r \frac{\partial \tilde{h}}{\partial t} = -r \frac{\partial q_z}{\partial z} - \frac{\partial (r q_r)}{\partial r} \quad (2.217)$$

Dividing by r and replacing \tilde{h} by $\bar{C}_p (T - T_{\text{ref}})$, where \bar{C}_p is the average heat capacity, and substituting the heat fluxes q with their corresponding relations (Fourier law):

$$q_z = -k_z \frac{\partial T}{\partial z} \quad (2.218)$$

and

$$q_r = -k_r \frac{\partial T}{\partial r} \quad (2.219)$$

Equation (2.217) is then equivalent to:

$$\rho \bar{C}_p \frac{\partial T}{\partial t} = k_z \frac{\partial^2 T}{\partial z^2} + \frac{k_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad (2.220)$$

This is a PDE where the temperature depends on three variables: t , z , and r . If we assume steady state conditions then the PDE becomes:

$$0 = k_z \frac{\partial^2 T}{\partial z^2} + \frac{k_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad (2.221)$$

If in addition to steady state conditions, the radius of the rod is assumed to be small so that the radial temperature gradient can be neglected then the PDE (Eq. 2.221) can be further simplified. In this case, the differential element upon which the balance equation is derived is a disk of thickness Δz and radius R . The heat conduction in the radial direction is omitted and replaced by the heat transfer through the surface area which is defined as follows:

$$Q = U(2\pi RL)(T_a - T) \quad (2.222)$$

Consequently, the above energy balance equation (Eq. 2.221) is reduced to the following ODE

$$0 = k_z \frac{d^2 T}{dz^2} - U(2\pi RL)(T_a - T) \quad (2.223)$$

2.2.5 Isothermal Plug Flow Reactor

Let consider a first-order reaction occurring in an isothermal tubular reactor as shown in figure 2.24. We assume plug flow conditions i.e. the density, concentration and velocity change with the axial direction only. Our aim is to develop a model for the reaction process in the tube.

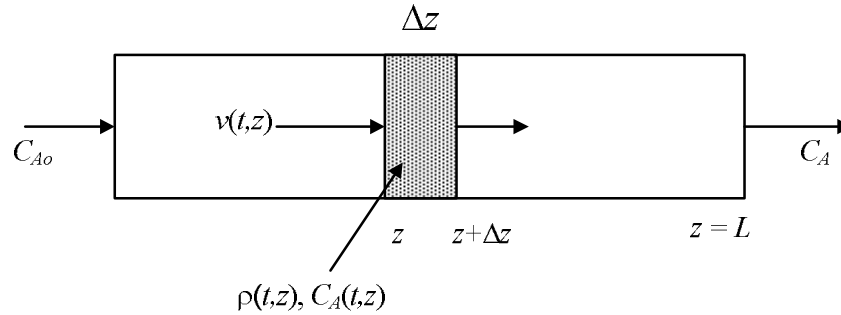


Figure 2-5 Isothermal Plug flow reactor

In the following we derive the microscopic component balance for species (A) around differential slice of width Δz and constant cross-section area (S).

Flow of moles of A in:

As has been indicated in section 1.11.1 mass transfer occurs by two mechanism; convection and diffusion. The flow of moles of species A into the shell is therefore the sum of two terms:

$$(vC_A S \Delta t) |_z + (N_A S \Delta t) |_z \quad (2.224)$$

where N_A is the diffusive flux of A (*moles of A/m² s*).

Flow of moles of A out:

$$(vC_A S \Delta t) |_{z+\Delta z} + (N_A S \Delta t) |_{z+\Delta z} \quad (2.225)$$

Accumulation:

$$(C_A S \Delta z) |_{t+\Delta t} - (C_A S \Delta z) |_t \quad (2.226)$$

Generation due to reaction inside the shell:

$$- r(S\Delta z\Delta t) \quad (2.227)$$

where $r = k C_A$ is the rate of reaction.

Substituting all the terms in the mass balance equation (Eq. 1.3) and dividing by Δt and Δz gives:

$$\frac{(C_A S)|_{t+\Delta t} - (C_A S)|_t}{\Delta t} = \frac{(vC_A S + N_A S)|_z - (vC_A S + N_A S)|_{z+\Delta z}}{\Delta z} - kC_A S \quad (2.228)$$

Taking the limit of $\Delta t \rightarrow 0$ and $\Delta z \rightarrow 0$ and omitting S from both sides give the following PDE:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial vC_A}{\partial z} - \frac{\partial N_A}{\partial z} - kC_A \quad (2.229)$$

where N_A is the molar flux given by Fick's law as follows:

$$N_A = -D_{AB} \frac{dC_A}{dz} \quad (2.230)$$

where D_{AB} is the binary diffusion coefficient. Equation 2.229 can be then written as follows:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial(vC_A)}{\partial z} + D_{AB} \frac{\partial^2 C_A}{\partial z^2} - kC_A \quad (2.231)$$

Expanding the derivatives, the last equation can be reduced to:

$$\frac{\partial C_A}{\partial t} = -v \frac{\partial C_A}{\partial z} - C_A \frac{\partial v}{\partial z} + D_{AB} \frac{\partial^2 C_A}{\partial z^2} - kC_A \quad (2.232)$$

This equation can be further simplified by using the mass balance equation for incompressible fluids (Eq. 2.189). We get then:

$$\frac{\partial C_A}{\partial t} = -v \frac{\partial C_A}{\partial z} + D_{Ab} \frac{\partial^2 C_A}{\partial z^2} - k C_A \quad (2.233)$$

The equation is a PDE for which the state variable (C_A) depends on both t and z .

The PDE is reduced at steady state to the following second order ODE,

$$0 = -v \frac{dC_A}{dz} + D_{Ab} \frac{d^2 C_A}{dz^2} - k C_A \quad (2.234)$$

The ODE can be solved with the following boundary conditions (BC):

$$\text{BC1:} \quad \text{at } z = 0 \quad C_A(0) = C_{A0} \quad (2.235)$$

$$\text{BC2:} \quad \text{at } z = L \quad \frac{dC_A(z)}{dz} = 0 \quad (2.236)$$

The first condition gives the concentration at the entrance of the reactor while the second condition indicates that there is no flux at the exit length of the reactor.

2.2.6 Non-Isothermal Plug-Flow reactor

The tubular reactor discussed earlier is revisited here to investigate its behavior under non-isothermal conditions. The heat of reaction is removed via a cooling jacket surrounding the reactor as shown in figure 2.25. Our objective is to develop a model for the temperature profile along the axial length of the tube. For this purpose we will need to write an energy balance around an element of the tubular reactor, as shown in Fig.2.25. The following assumptions are made for the energy balance:

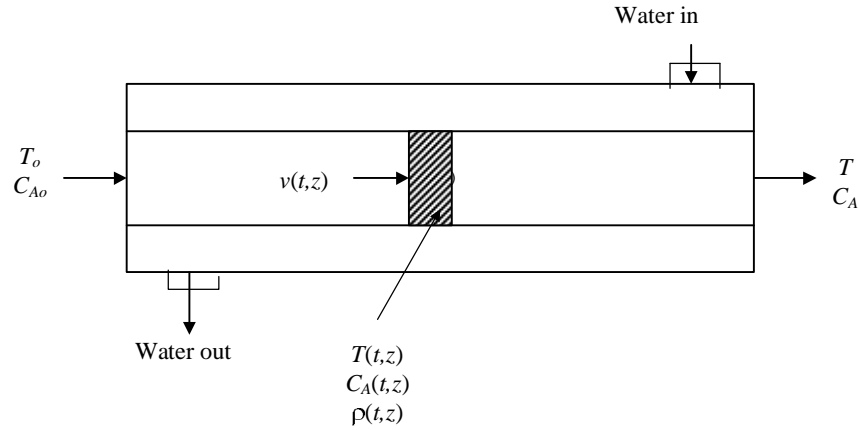


Figure 2-25 Non-isothermal plug flow reactor

Assumptions:

- Kinetic and potential energies are neglected.
- No Shaft work
- Internal energy is approximated by enthalpy
- Energy flow will be due to bulk flow (convection) and conduction.

Under these conditions, the microscopic balance around infinitesimal element of width Δz with fixed cross-section area is written as follows:

Energy flow into the shell:

As mentioned in Section 1.11.3 the flow of energy is composed of a term due to convection and another term due to molecular conduction with a flux q_z .

$$(q_z A + v A \rho \tilde{h}) \Delta t|_z \quad (2.237)$$

Energy flow out of the shell:

$$(q_z A + v A \rho \tilde{h}) \Delta t|_{z+\Delta z} \quad (2.238)$$

Accumulation of energy:

$$(\rho A \tilde{h} \Delta z)|_{t+\Delta t} - (\rho A \tilde{h} \Delta z)|_t \quad (2.239)$$

Heat generation by reaction:

$$(-\Delta H_r)kC_A A \Delta z \Delta t \quad (2.240)$$

Heat transfer to the wall:

$$h_t(\pi D \Delta z)(T - T_w)\Delta t \quad (2.241)$$

where h_t is film heat transfer coefficient.

Substituting these equations in the conservation law (equation 1.7) and dividing by $A \Delta t \Delta z$ give:

$$\begin{aligned} \frac{(\rho \tilde{h})|_{t+\Delta t} - (\rho \tilde{h})|_t}{\Delta t} &= \frac{(\rho v \tilde{h})|_z - (\rho v \tilde{h})|_{z+\Delta z}}{\Delta z} + \frac{q_z|_z - q_z|_{z+\Delta z}}{\Delta z} \\ &\quad - \Delta H_r k C_A - h_t \left(\frac{\pi D}{A} \right) (T - T_w) \end{aligned} \quad (2.242)$$

Taking the limit as Δt and Δz go to zero yields:

$$\frac{\partial(\rho \tilde{h})}{\partial t} = -\frac{\partial(\rho v \tilde{h})}{\partial z} - \frac{\partial q_z}{\partial z} - \Delta H_r k C_A - h_t \left(\frac{\pi D}{A} \right) (T - T_w) \quad (2.243)$$

The heat flux is defined by Fourier's law as follows:

$$q_z = -k_t \frac{\partial T}{\partial z} \quad (2.244)$$

where k_t is the thermal conductivity. The specific enthalpy (\tilde{h}) can be approximated by:

$$\tilde{h} = \bar{C}_p (T - T_{ref}) \quad (2.245)$$

Since the fluid is incompressible it satisfies the equation of continuity (Eq. 2.189).

Substituting these expressions in Eq. 2.243 and expanding gives:

$$\rho \bar{C}_p \frac{\partial T}{\partial t} = -\rho \bar{C}_p v \frac{\partial T}{\partial z} + k_t \frac{\partial^2 T}{\partial z^2} - \Delta H_r k_o e^{-E/RT} C_A - h_i \left(\frac{\pi D}{A} \right) (T - T_w) \quad (2.246)$$

At steady state this PDE becomes the following ODE,

$$0 = -\rho \bar{C}_p v \frac{dT}{dz} + k_t \frac{d^2 T}{dz^2} - \Delta H_r k_o e^{-E/RT} C_A - h_i \left(\frac{\pi D}{A} \right) (T - T_w) \quad (2.247)$$

Similarly to Eq. 2.234 we could impose the following boundary conditions:

$$\text{B.C1:} \quad \text{at } z = 0 \quad T(z) = T_o \quad (2.248)$$

$$\text{B.C2:} \quad \text{at } z = L \quad \frac{dT(z)}{dz} = 0 \quad (2.249)$$

The first condition gives the temperature at the entrance of the reactor and the second condition indicates that there is no flux at the exit length of the reactor.

2.2.7 Heat Exchanger: Distributed parameter model

We revisit the shell-and-tube heat exchanger already discussed in example 2.1.6. Steam of known temperature T_s flowing around the tube is heating a liquid L of density ρ_L and constant velocity v from temperature T_{L1} to T_{L2} . The temperature in the tube varies obviously with axial direction z , radial direction r and time t . To simplify the problem we will assume that there are no change in the radial direction. This assumption is valid if the radius is small and no large amount of heat is transferred. The heat transfer from the steam to the liquid depends on the heat transfer coefficient on the steam side, h_{to} and on the transfer on the liquid side h_{ti} . We also neglect the thermal capacity of the metal wall separating the steam and the liquid and assume that the exchange between the steam and liquid occurs with an overall heat transfer coefficient U . We also assume constant heat capacity for the liquid. An energy balance on a differential element of the exchanger of length Δz and cross-sectional area A , yields:

Flow of energy in:

$$(vA\rho \bar{C}_p)\Delta t|_z \quad (2.250)$$

Flow of energy out:

$$(vA\rho \bar{C}_p)\Delta t|_{z+\Delta z} \quad (2.251)$$

Energy accumulation:

$$(A\rho \tilde{h} \Delta z)|_{t+\Delta t} - (A\rho \tilde{h} \Delta z)|_t \quad (2.252)$$

Energy generated:

$$U(\pi D \Delta z)(T - T_s)\Delta t \quad (2.253)$$

Using the expression for specific enthalpy (Eq. 2.245) and dividing by $A\Delta t\Delta z$, the energy balance yields:

$$\frac{(\rho A \bar{C}_p (T - T_{ref}) \Delta z)|_{t+\Delta t} - (\rho A \bar{C}_p (T - T_{ref}) \Delta z)|_t}{\Delta t} = \frac{(vA\rho \bar{C}_p T)|_z - (vA\rho \bar{C}_p T)|_{z+\Delta z}}{\Delta z} - U\left(\frac{\pi D}{A}\right)(T - T_s) \quad (2.254)$$

Taking the limit as Δt and Δz goes to zero gives:

$$\frac{\partial(\rho A \bar{C}_p T)}{\partial t} = -\frac{\partial(vA\rho \bar{C}_p T)}{\partial z} - U\left(\frac{\pi D}{A}\right)(T - T_s) \quad (2.255)$$

Since $A = \pi D^2/4$ and dividing by $\rho \bar{C}_p$ Eq. (2.255) is equivalent to:

$$\frac{\partial T}{\partial t} = -v \frac{\partial T}{\partial z} - \left(\frac{4U}{\rho \bar{C}_p D}\right)(T - T_s) \quad (2.256)$$

At steady state the PDE becomes the following ODE,

$$0 = -v \frac{dT}{dz} - \left(\frac{4U}{\rho \bar{C}_p D} \right) (T - T_s) \quad (2.257)$$

With the following condition:

$$T(z = 0) = T_0 \quad (2.258)$$

2.2.8 Mass exchange in packed column

In previous section (section 2.1.12) we presented some examples of mass transfer units that can be described by simple ODE's. This includes all the operations that can occur in tray or spray-tray towers. In this section we present an example of modeling a mass transfer operation that occurs in packed tower. Absorption is a mass transfer process in which a vapor solute (*A*) in a gas mixture is absorbed by contact with a liquid phase in which the solute is more or less soluble. The gas phase consists usually of an inert gas and the solute. This process involves flow transfer of the solute *A* through a stagnant non diffusive gas *B* into a stagnant liquid *C*. The liquid is mainly immiscible in the gas phase. An example is the absorption of ammonia (*A*) from air (*B*) by liquid water (*C*). The operation can be carried out either in tray (plate) towers or in packed towers. The operation in tray towers can be modeled similarly to the liquid-liquid extraction process in Example 2.1.12 and it is left as an exercise. We consider here the absorption taking place in a packed tower.

Consider the binary absorption tower shown in Figure 2.26. A liquid stream flow downward with molar flow rate *L* and feed composition (*X_{Af}*). Vapor stream flows upward with molar flow rate (*G*) and feed composition (*Y_{Af}*). A simple vapor-liquid equilibrium relation of the form of:

$$Y_A = HX_A \quad (2.265)$$

is used, where *H* (mole fraction gas/mole fraction liquid) is the Henry's law constant. This assumption is valid for dilute streams. The molar rates can be considered constants,

i.e. not changing from one stage to another, thus the total mass balance need not be written. To establish the model equations we need to write equations for liquid and vapor phase. To simplify the problem we assume constant liquid and vapor holdup in each stage. We also assume isothermal conditions. An energy balance therefore is not needed.

The flux N_A transferred from bulk liquid to bulk gas is given by:

$$N_A = K_Y (Y_A - Y_A^*) \quad (2.266)$$

Where K_Y is the overall mass transfer in the gas-phase ($kgmole/m^2s$ mole fraction) and Y_A^* is the value that would be in equilibrium with X_A . The flux can also be expressed as:

$$N_A = K_X (X_A - X_A^*) \quad (2.267)$$

Where K_X is the overall mass transfer coefficient in the liquid-phase and X_A^* is the value that would be in equilibrium with Y_A .

A mass balance on the liquid phase for a differential volume (Fig. 2.26) of the column length z and cross sectional area S yields:

Flow of mole in:

$$[(SLX_A)\Delta t]_z + (N_A S \Delta t)|_z \Delta z \quad (2.268)$$

Flow of moles out:

$$(SLX_A)\Delta t|_{z+\Delta z} \quad (2.269)$$

Rate of accumulation:

$$(SH_L X_A \Delta z)|_{t+\Delta t} - (SH_L X_A \Delta z)|_t \quad (2.270)$$

where X_A is the liquid fraction of A and H_L the liquid holdup ($mole/m^3$).

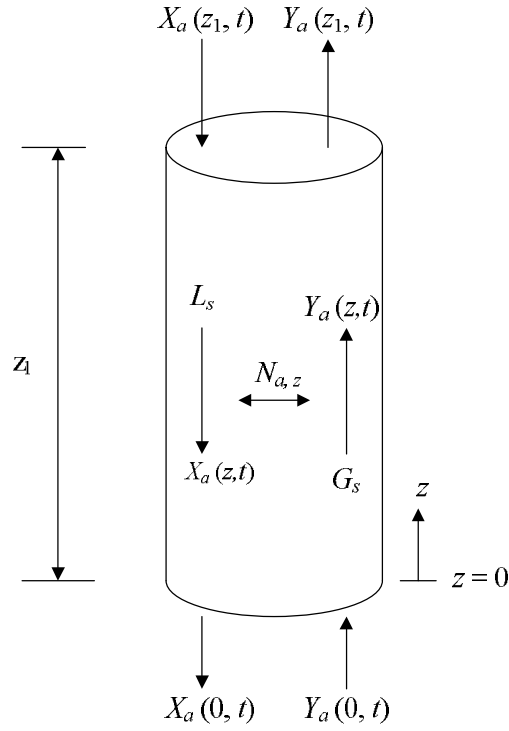


Figure 2-26 Packed column

The balance equation yields:

$$(SH_L X_A \Delta z)|_{t+\Delta t} - (SH_L X_A \Delta z)|_t = (SLX_A)\Delta t|_{z+\Delta z} - [(SLX_A)\Delta t|_z + (N_A S \Delta t)\Delta t|_z] \Delta z \quad (2.271)$$

Dividing by $S \Delta t \Delta z$ and taking the limits as Δz and Δt goes to zero yield:

$$H_L \frac{\partial X_A}{\partial t} = L \frac{\partial X_A}{\partial z} + N_A \quad (2.272)$$

which is equivalent to

$$H_L \frac{\partial X_A}{\partial t} = L \frac{\partial X_A}{\partial z} + K_Y (Y_A - Y_A^*) \quad (2.273)$$

We could also use the expression of flux (Eq. 2.267):

$$H_L \frac{\partial X_A}{\partial t} = L \frac{\partial X_A}{\partial z} + K_X (X_a^* - X_A) \quad (2.274)$$

We can develop material balances for the gas phase that are similar to Eq. 2.274. This gives:

$$H_G \frac{\partial X_A}{\partial t} = -G \frac{\partial Y_A}{\partial z} + K_Y (Y_A - Y_A^*) \quad (2.275)$$

or alternatively:

$$H_G \frac{\partial Y_A}{\partial t} = -G \frac{\partial Y_A}{\partial z} + K_X (X_a^* - X_A) \quad (2.276)$$

It should be noted that the analysis carried here can be used for a number of operations where packed columns are used. This includes liquid-liquid extraction, gas-liquid absorption and gas-solid drying. In each of these operations an equilibrium relation of the type:

$$Y_A = f(X_A) \quad (2.277)$$

is generally available.

