UNIT III MODELING OF REACTORS

3.INTRODUCTION

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 were 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.

3.1 LIQUID STORAGE TANK

Consider the perfectly mixed storage tank shown in figure 3.1. 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.

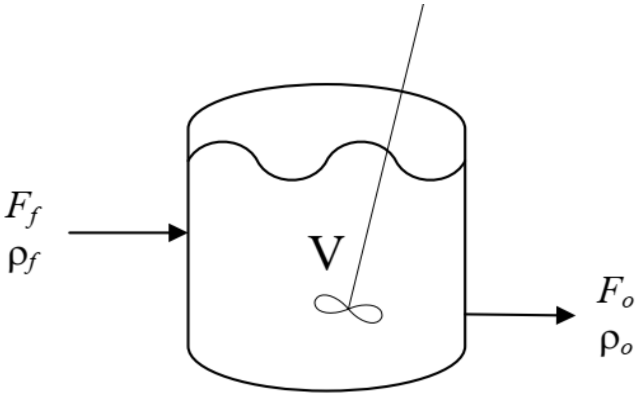

Figure 3.1 Liquid Storage Tank

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 to the total mass $m = \rho V$. This yields:

Mass flow in:

$$\rho_f F_f \tag{3.1}$$

Mass flow out:

$$\rho_o F_o \tag{3.2}$$

Accumulation:

$$\frac{dm}{dt} = \frac{d(\rho V)}{dt} \tag{3.3}$$

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

$$\rho_f F_f = \rho_o F_o + \frac{d(\rho V)}{dt} \tag{3.4}$$

For consistency we can check that all the terms in the equation have the SI unit of *kg/s*. The resulting model (Eq. 3.4) 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.

$$V(t_i) = V_i \tag{3.5}$$

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. 3.4 is reduced to:

$$\frac{dV}{dt} = F_f - F_o \tag{3.6}$$

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

$$V = AL \tag{3.7}$$

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

$$A\frac{dL}{dt} = F_f - F_o \tag{3.8}$$

with initial condition:

$$L(t_i) = L_i \tag{3.9}$$

Degree of freedom analysis

For the system described by Eq. 3.8 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. 3.8)

Therefore the degree of freedom is:

Number of remaining variables – 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:

$$F_o = \alpha\sqrt{L} \tag{3.10}$$

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:

$$F_o = F_o(L,L_s) \tag{3.11}$$

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

$$F_o = K_c(L - L_s) + F_{ob} \tag{3.12}$$

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:

$$F_0 = F_f \tag{3.13}$$

3.2 ISOTHERMAL CSTR

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

$$A \xrightarrow{k} B \qquad (3.14)$$

The reaction is assumed to be irreversible and of first order. As shown in figure 3.2, 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_0 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 3.1 still hold and the total mass balance equation (Eq. 3.6) is therefore unchanged

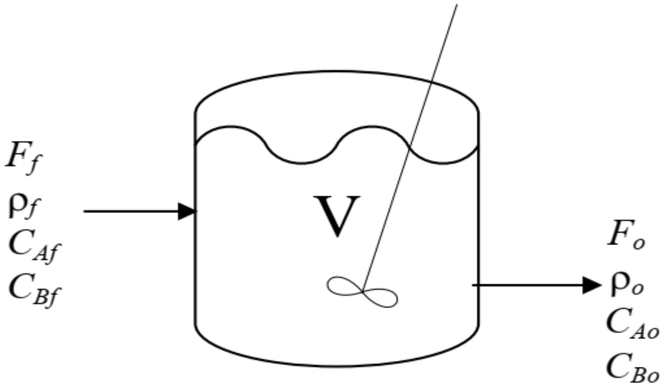

Figure 3.2 Isothermal CSTR

The component balance on species A is obtained by the application of law of conservation of mass 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:

$$F_f\, C_{Af} \qquad (3.15)$$

Flow of moles of *A* out:

$$F_o\, C_{Ao} \qquad (3.16)$$

Rate of accumulation:

$$\frac{dn}{dt} = \frac{d(VC_A)}{dt} \tag{3.17}$$

Rate of generation: $-rV$

where r (*moles/m*^{3}*s*) is the rate of reaction.

Substituting these terms in the general equation yields:

$$\frac{d(VC_A)}{dt} = F_f\ C_{Af} - F_o\ C_A - rV \tag{3.18}$$

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 (3.18) can be written as follows:

$$\frac{d(VC_A)}{dt} = V\frac{d(C_A)}{dt} + C_A\frac{d(V)}{dt} = F_f\ C_{Af} - F_o\ C_A - rV \tag{3.19}$$

Substituting Equation (3.6) into (3.19) and with some algebraic manipulations we obtain:

$$V\frac{d(C_A)}{dt} = F_f(\ C_{Af} - C_A) - rV \tag{3.20}$$

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

$$r = k\ C_A \tag{3.21}$$

Equations 3.6 and 3.20 define the dynamic behavior of the reactor. They can be solved if the system is exactly specified and if the initial conditions are given:

$$V(t_i) = V_i \text{ and } C_A(t_i) = C_{Ai} \tag{3.22}$$

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. 3.6 and Eq. 3.20)

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. 3.10) or in closed loop operation (Eq. 3.11).

The steady state behavior can be simply obtained by setting the accumulation terms to zero. Equation 3.6 and 3.20 become:

$$F_0 = F_f \tag{3.23}$$

$$F_f(\, C_{Af} - C_A) = rV \tag{3.24}$$

3.3 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:

$$A \leftrightarrow 2B \tag{3.25}$$

taking place in perfectly mixed vessel sketched in figure 3.3. 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.

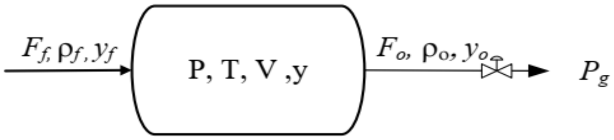

Figure 3.3 Gas Pressurized Reactor

Writing the macroscopic total mass balance around the vessel gives:

$$\frac{d(\rho V)}{dt} = \rho_f F_f - \rho_o F_o \qquad (3.26)$$

Since *V* is constant we have:

$$V\frac{d\rho}{dt} = \rho_f F_f - \rho_o F_o \qquad (3.27)$$

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

$$V\frac{dC_A}{dt} = F_f C_{Af} - F_o C_{A_0} - r_1 V + r_2 V \qquad (3.28)$$

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

$$r_1 = k_1\ C_A \qquad (3.29)$$

$$r_2 = k_2 C_B{}^2 \qquad (3.30)$$

Equations (3.27) and (3.28) 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:

$$C_A = yP/RT \qquad (3.31)$$

$$C_B = (1 - y)P/RT \tag{3.32}$$

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

$$\rho = MP/RT = [M_A y + M_B\,(1 - y)]P/RT \tag{3.33}$$

Where M_A and M_B are the molecular weight of A and B respectively. Therefore one can substitute equations (3.31) to (3.33) into equations (3.27 & 3.28) 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
- The degree of freedom is therefore 6 − 5 =1. The extra relation relates the outlet flow to the pressure as follows:

$$F_o = C_v \sqrt{\frac{P - P_g}{\rho}} \tag{3.34}$$

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

3.4 NON-ISOTHERMAL CSTR

We reconsider the previous CSTR example but for non-isothermal conditions. The reaction A → B is exothermic and the heat generated in the reactor is removed via a cooling system as shown in figure 3.4. The effluent temperature is different from the inlet temperature due to heat generation by the exothermic reaction.

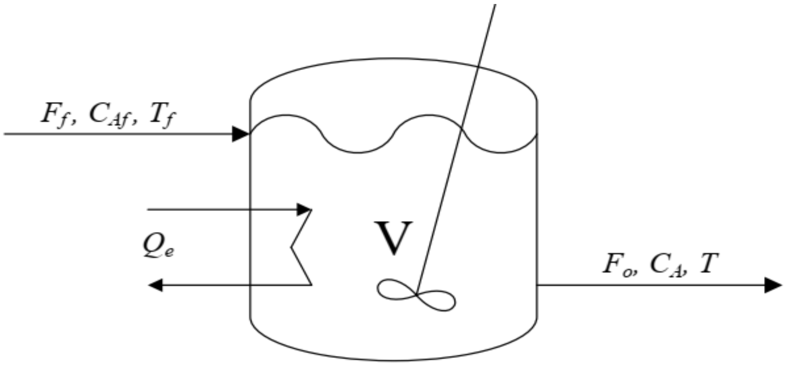

Figure 3.4 Non-isothermal CSTR

Assuming constant density, the macroscopic total mass balance (Eq. 3.6) and mass component balance remain the same as before. However, one more ODE will be produced from the applying the conservation law for total energy balance. The dependence of the rate constant on the temperature:

$$k = k_o e^{-E/RT} \tag{3.35}$$

should be emphasized.

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

$$\rho\widetilde{C}_p \frac{d\left(V(T-T_{ref})\right)}{dt} = \rho F_f \widetilde{C}_p (T_f - T_{ref}) - \rho F_o \widetilde{C}_p (T - T_{ref}) + Q_r - Q_e \tag{3.36}$$

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 $T_{\text{ref}} = 0$ for simplicity and using the differentiation principles, equation 3.36 can be written as follows:

$$\rho\widetilde{C}_p V \frac{dT}{dt} + \rho\widetilde{C}_p T \frac{dV}{dt} = \rho F_f \widetilde{C}_p T_f - \rho F_o \widetilde{C}_p T + Q_r - Q_e \tag{3.37}$$

Substituting Equation 3.6 into the last equation and rearranging yields:

$$\rho\widetilde{C}_p V \frac{dT}{dt} = \rho F_f \widetilde{C}_p (T_f - T) + Q_r - Q_e \tag{3.38}$$

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

$$Q_r = -(\Delta H_r)Vr \tag{3.39}$$

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:

$$\frac{dV}{dt} = F_f - F_o \tag{3.40}$$

$$V\frac{d(C_A)}{dt} = F_f(\, C_{Af} - C_A) - rV \tag{3.41}$$

$$\rho\widetilde{C}_p V\frac{dT}{dt} = \rho F_f \widetilde{C}_p (T_f - T) + (-\Delta H_r)Vr - Q_e \tag{3.42}$$

where the rate (r) is given by:

$$r = k_o e^{-E/RT} C_A \tag{3.43}$$

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

$$V(t_i) = V_i \qquad T(t_i) = T_i \qquad \text{and} \qquad C_A(t_i) = C_{Ai} \tag{3.44}$$

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

  The degree of freedom is $5-3 = 2$. Following the analysis of example 3.3, 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. 3.5). 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:

$$\rho_j \tilde{C}_{p_j} V_j \frac{dT_j}{dt} = \rho_j F_j \tilde{C}_{p_j} (T_{jf} - T_j) + Q_e \tag{3.45}$$

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.

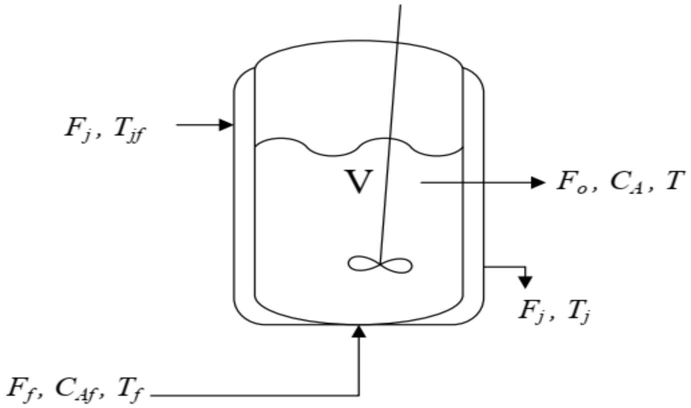

Figure 3.5 Jacketed Non-isothermal CSTR

3.5 TWO-PHASE REACTOR

Consider the two phase reactor shown in figure 3.6. 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.

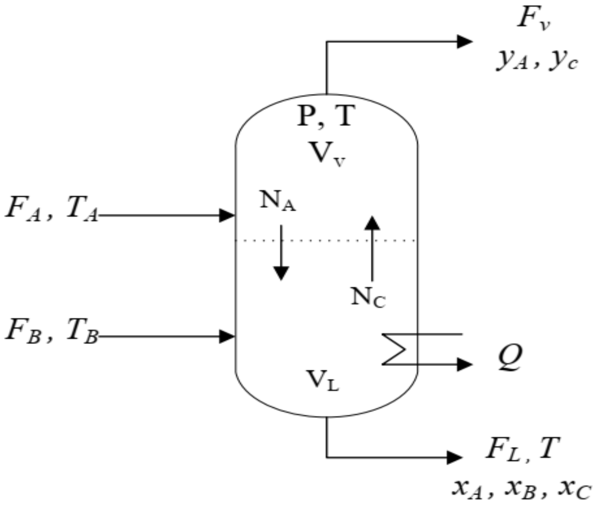

Figure 3.6 Two Phase Reactor

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 Cp, 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:

$$\frac{dN_v}{dt} = F_A - N_A + N_c - F_v \tag{3.46}$$

Component balance for A:

$$\frac{d(N_v y_A)}{dt} = F_A - N_A - F_v y_A \tag{3.47}$$

Since $d(N_v y_A)/dt = N_v\, dy_A/dt + y_A\, dN_v/dt$, and using equation (3.46), equation (3.47) can be written as follows:

$$N_v \frac{dy_A}{dt} = F_A(1 - y_A) - N_A(1 - y_A) - N_c y_A \tag{3.48}$$

Liquid phase:

Total mass balance:

$$\frac{dN_L}{dt} = F_B + N_A - N_c - F_L - R_c \tag{3.49}$$

Component balance for A:

$$\frac{d(N_L x_A)}{dt} = N_A - F_L x_A - R_c \tag{3.50}$$

Since $d(N_L\, x_A)/dt = N_L\, dx_A/dt + x_A\, dN_L/dt$, and using equation (3.49), equation (3.50) can be written as follows:

$$N_L \frac{dx_A}{dt} = N_A(1 - x_A) - F_B x_A - R_c(1 - x_A) + N_c x_A \tag{3.51}$$

Component balance for B:

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

$$N_L \frac{dx_B}{dt} = N_A(1-x_B) + F_B x_B - R_c(1-x_B) + N_c x_B \tag{3.52}$$

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

$$\frac{d(N_L H_L + N_v H_v)}{dt} = F_B Cp T_B + F_A(Cp T_A + \lambda) - F_L Cp T - F_v Cp T - R_c \Delta H_r + Q \tag{3.53}$$

Note that:

$$\frac{d(N_L H_L)}{dt} = N_L \frac{d(H_L)}{dt} + H_L \frac{d(N_L)}{dt} = N_L Cp \frac{d(T)}{dt} + Cp T \frac{d(N_L)}{dt} \tag{3.54}$$

$$\frac{d(N_v H_v)}{dt} = N_v \frac{d(H_v)}{dt} + H_v \frac{d(N_v)}{dt} = N_v Cp \frac{d(T)}{dt} + (Cp T + \lambda) \frac{d(N_v)}{dt} \tag{3.55}$$

Substituting the last two equations, and using the definition of dN_L/dt and dN_v/dt from equations (3.46) and (3.49), in equation (3.55) yields:

$$N_L + N_v \frac{d(T)}{dt} = F_A(T_A - T) + F_B(T_B - T) + R_c(T - \frac{\Delta H_r}{Cp}) + \frac{\lambda}{Cp}(N_A - N_c) + \frac{Q}{Cp} \tag{3.56}$$

The following additional equations are needed:

Vapor-liquid equilibrium relations:

$$y_A P - x_A P_A^s = 0 \tag{3.57}$$

$$y_A P - (1 - x_A - x_B) P_c^s = 0 \tag{3.58}$$

Total volume constraint:

$$V = V_L + V_v \tag{3.59}$$

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

$$nRT = N_vRT + N_LP/\rho \tag{3.60}$$

or

$$V = N_vRT/P + N_L/\rho \tag{3.61}$$

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: 9
- The degree is 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.

3.6 REACTION WITH MASS TRANSFER

Figure 3.7 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 of the top of the vessel. The reaction mechanism is given as follows:

$$A + B \rightarrow C \tag{3.62}$$

Assumptions:

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

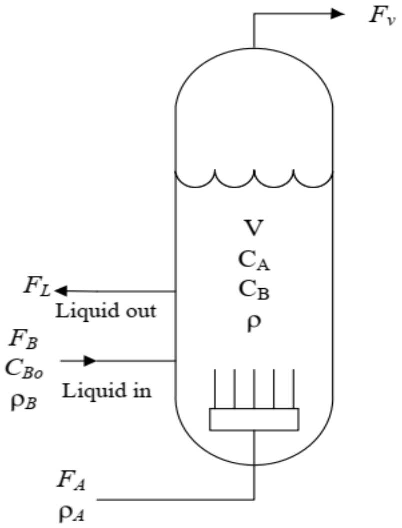

Figure 3.7 Reaction with Mass Transfer

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:

$$N_A = K_L\,(C^*_A - C_A) \tag{3.63}$$

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:

$$\frac{d\rho V}{dt} = \rho_B F_B + M_A A_m N_A - \rho F_L \tag{3.64}$$

Component balance on A:

$$V\frac{dC_A}{dt} = A_m N_A - F_L C_A - rV \tag{3.65}$$

Component balance on B:

$$V\frac{dC_B}{dt} = F_B C_{Bo} - F_L C_B - rV \tag{3.66}$$

Vapor phase:

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

$$F_v = F_A - M_A\, A_m\, N_A/\rho_A \tag{3.67}$$

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, ρ, ρ_A, ρ_B,
- Remaining variables: C_B, N_A, C_A, F_v, V
- Number of equations: (Eq. 3.63-3.67)

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.

3.7 ISOTHERMAL PLUG FLOW REACTOR

Let consider a first-order reaction occurring in an isothermal tubular reactor as shown in figure 3.8. 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.

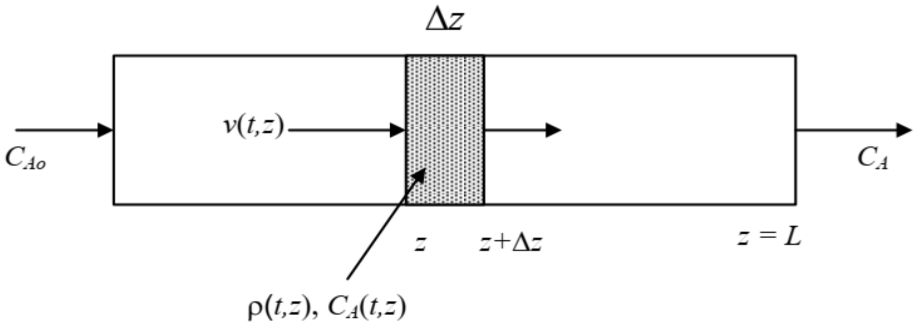

Figure 3.8 Isothermal Plug flow reactor

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:

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:

$$(vC_A\,S\,\Delta t)\,|_z + (N_A\,S\,\Delta t)|_z \tag{3.68}$$

where N_A is the diffusive flux of A ($moles\ of\ A/m^2\ s$).

Flow of moles of A out:

$$(vC_A\,S\,\Delta t)\,|_{z+\Delta z} + (N_A\,S\,\Delta t)|_{z+\Delta z} \tag{3.69}$$

Accumulation:

$$(C_A\, S\, \Delta z)\,|_{t+\Delta t} - (C_A\, S\, \Delta z)\,|_t \tag{3.70}$$

Generation due to reaction inside the shell:

$$-\, r(S\Delta z\Delta t) \tag{3.71}$$

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

Substituting all the terms in the mass balance equation and dividing by Δt and Δz gives:

$$\frac{(C_A S)\,|_{t+\Delta t} - (C_A S)\,|_t}{\Delta t} = \frac{(vC_A S + N_A S)\,|_z - (vC_A S + N_A S)\,|_{z+\Delta z}}{\Delta z} - kC_A S \tag{3.72}$$

Taking the limit of Δt → 0 and Δz → 0 and omitting S from both sides give the following PDE:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial v C_A}{\partial z} - \frac{\partial N_A}{\partial z} - kC_A \tag{3.73}$$

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

$$N_A = -D_{AB}\frac{dC_A}{dz} \tag{3.74}$$

where D_{AB} is the binary diffusion coefficient. Equation 3.73 can be then written as follows:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial (vC_A)}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A \tag{3.75}$$

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

$$\frac{\partial C_A}{\partial t} = -v\frac{\partial C_A}{\partial z} - C_A\frac{\partial v}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A \tag{3.76}$$

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

$$\frac{\partial C_A}{\partial t} = -v\frac{\partial C_A}{\partial z} + D_{Ab}\frac{\partial^2 C_A}{\partial z^2} - kC_A \tag{3.77}$$

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,

$$0 = -v\frac{dC_A}{dz} + D_{Ab}\frac{d^2 C_A}{dz^2} - kC_A \tag{3.78}$$

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

BC1: at $z = 0$ $C_A(0) = C_{A0}$ (3.79)
BC2: at $z = L$ $\frac{dC_A(z)}{dz} = 0$ (3.80)

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.

3.8 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 3.9. 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.3.9. The following assumptions are made for the energy balance:

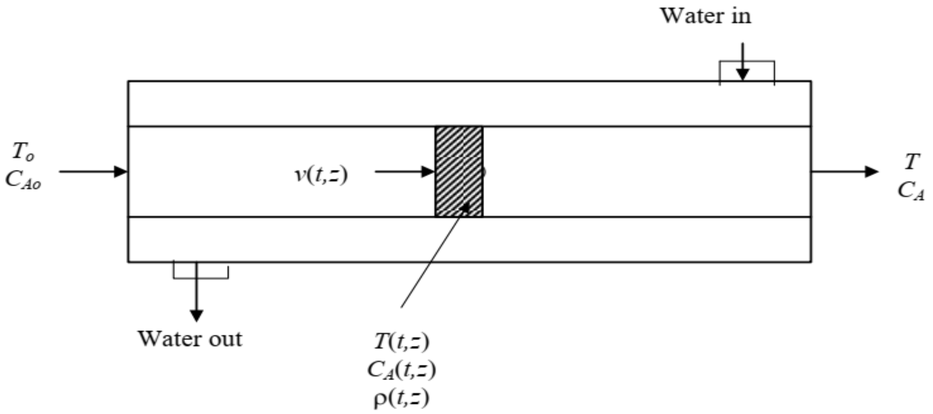

Figure 3.9 Non-isothermal plug flow reactor

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:

The flow of energy is composed of a term due to convection and another term due to molecular conduction with a flux q_z.

$$(q_z A + v A\rho \tilde{h})\Delta t|_z \tag{3.81}$$

Energy flow out of the shell:

$$(q_z A + v A\rho \tilde{h})\Delta t|_{z+\Delta z} \tag{3.82}$$

Accumulation of energy:

$$(\rho A \tilde{h}\, \Delta z)|_{t+\Delta t} - (\rho A \tilde{h}\, \Delta z)|_t \tag{3.83}$$

Heat generation by reaction:

$$(-\Delta H_r)kC_A\, A\, \Delta z\, \Delta t \tag{3.84}$$

Heat transfer to the wall:

$$h_t(\pi D\Delta z)(T - T_w)\Delta t \tag{3.85}$$

where h_t is film heat transfer coefficient.

Substituting these equations in the conservation law and dividing by $A\Delta t\, \Delta z$ give:

$$\frac{(\rho\tilde{h})|_{t+\Delta t} - (\rho\tilde{h})|_t}{\Delta t} = \frac{(\rho v\tilde{h})|_z - (\rho v\tilde{h})|_{z+\Delta z}}{\Delta z} + \frac{q_z|_z - q_z|_{z+\Delta z}}{\Delta z} - \Delta H_r kC_A - h_t(\frac{\pi D}{A})(T - T_w) \tag{3.86}$$

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

$$\frac{\partial(\rho\tilde{h})}{\partial t} = -\frac{\partial(\rho v\tilde{h})}{\partial z} - \frac{\partial q_z}{\partial z} - \Delta H_r kC_A - h_t(\frac{\pi D}{A})(T - T_w) \tag{3.87}$$

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

$$q_z = -k_t\frac{\partial T}{\partial z} \tag{3.88}$$

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

$$\tilde{h} = \overline{C}p(T - T_{ref}) \tag{3.89}$$

Since the fluid is incompressible it satisfies the equation of continuity .Substituting these expressions in Eq. 3.87 and expanding gives:

$$\rho \bar{C}p \frac{\partial T}{\partial t} = -\rho \bar{C}pv \frac{\partial T}{\partial z} + k_t \frac{\partial^2 T}{\partial z^2} - \Delta H_r k_o e^{-E/RT} C_A - h_t (\frac{\pi D}{A})(T - T_w) \tag{3.90}$$

At steady state this PDE becomes the following ODE,

$$0 = -\rho \bar{C}pv \frac{dT}{dz} + k_t \frac{d^2 T}{dz^2} - \Delta H_r k_o e^{-E/RT} C_A - h_t (\frac{\pi D}{A})(T - T_w) \tag{3.91}$$

Similarly to Eq. 3.78 we could impose the following boundary conditions:

B.C1: at $z = 0$ $T(z) = T_o$ (3.92)

B.C2: at $z = L$ $\frac{dT(z)}{dz} = 0$ (3.93)

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.