UNIT IV MODELING OF HEAT AND MASS TRANSFER OPERATIONS

4.1 HEAT EXCHANGER

Consider the shell and tube heat exchanger shown in figure 4.1. 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.

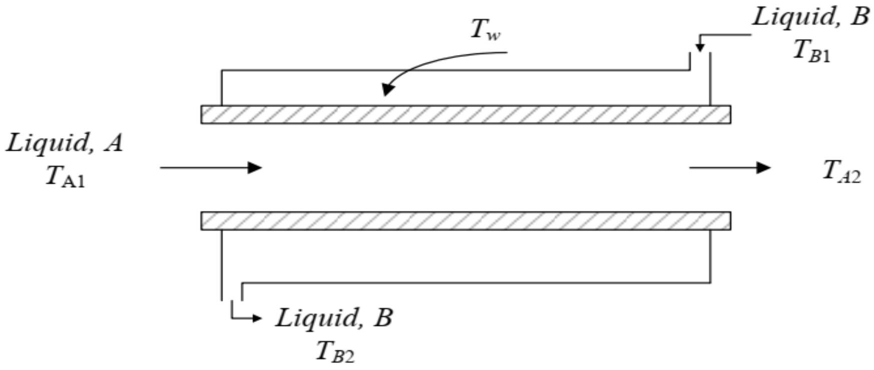

Figure 4-1 Heat Exchanger

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:

$$T_A = \frac{T_{A1} + T_{A2}}{2} \tag{4.1}$$

$$T_B = \frac{T_{B1} + T_{B2}}{2} \tag{4.2}$$

For liquid *A,* a macroscopic energy balance yields:

$$\rho_A C_{p_A} V_A \frac{dT_A}{dt} = \rho_A F_A C_{p_A} (T_{A1} - T_{A2}) + Q \tag{4.3}$$

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

$$\rho_B C_{p_B} V_B \frac{dT_B}{dt} = \rho_B F_B C_{p_B} (T_{B1} - T_{B2}) - Q \tag{4.4}$$

The amount of heat Q exchanged is:

$$Q = UA_H (T_B - T_A) \tag{4.5}$$

Or using the log mean temperature difference:

$$Q = UA_H \Delta T_{lm} \tag{4.6}$$

where

$$\Delta T_{lm} = \frac{(T_{A2} - T_{B1}) - (T_{A1} - T_{B2})}{\ln \frac{(T_{A2} - T_{B1})}{(T_{A1} - T_{B2})}} \tag{4.7}$$

with U ($J/m^2 s$) 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. 4.3) and (Eq. 4.4) and the algebraic equation (Eq. 4.5).

Degrees of freedom analysis

- Parameter of constant values: ρ_A, Cp_A, V_A, ρ_B, Cp_B, 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. 4.3, 4.4, 4.5)

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 Cp_w. 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:

$$\rho_B C_{p_B} V_B \frac{dT_B}{dt} = \rho_B F_B C_{p_B}(T_{B1} - T_{B2}) - h_{o,t} A_{o,t}(T_B - T_W) \tag{4.8}$$

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

$$\rho_w C_{p_w} V_w \frac{dT_w}{dt} = h_{o,t} A_{o,t}(T_B - T_w) - h_{i,t} A_{i,t}(T_w - T_A) \tag{4.9}$$

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

$$\rho_A C_{p_A} V_A \frac{dT_A}{dt} = \rho_A F_A C_{p_A}(T_{A1} - T_{A2}) + h_{i,t} A_{i,t}(T_w - T_A) \tag{4.10}$$

Note that the introduction of equation (Eq.4.9) 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 4.2). If the pressure of the steam changes then we need to write both mass and energy balance equations on the steam side.

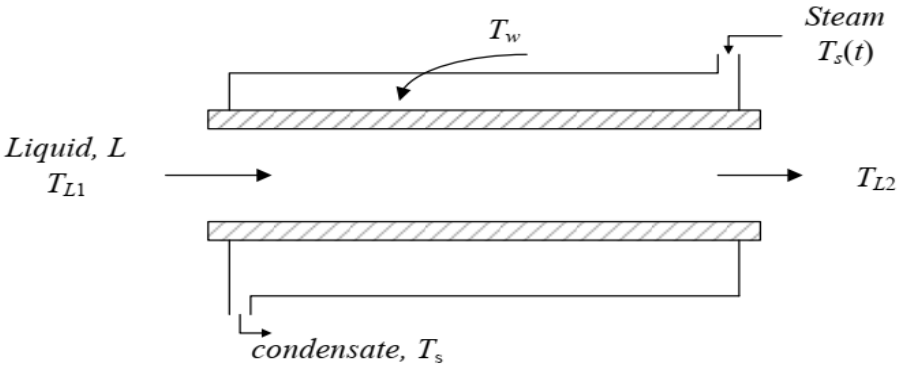

Figure 4.2 Heat Exchanger with Heating Steam

The energy balance on the tube side gives:

$$\rho_L C_{p_L} V_L \frac{dT_L}{dt} = \rho_L F_L C_{p_L} (T_{L1} - T_{L2}) + Q_s \tag{4.11}$$

where

$$T_L = \frac{T_{L1} + T_{L2}}{2} \tag{4.12}$$

$$Q_s = UA_s\,(T_s - T_L) \tag{4.13}$$

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

$$T_s = T_s\,(P) \tag{4.14}$$

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

$$m_S = \frac{M_S P_S V_S}{R T_S} \tag{4.15}$$

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

$$\frac{M_S V_S}{R T_S}\frac{dP}{dt} = \rho_S F_S - \rho_C F_C \tag{4.16}$$

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:

$$Q_s = F_c \, \lambda_s \tag{4.17}$$

Where λ_s is the latent heat.

Degrees of freedom analysis

- Parameter of constant values: ρ_L, Cp_L, 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. 4.11, 4.13, 4.14, 4.16, 4.17)

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.

4.2 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 4.3. The feed consists of N_c components with the molar fraction z_i (i=1,2… 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.

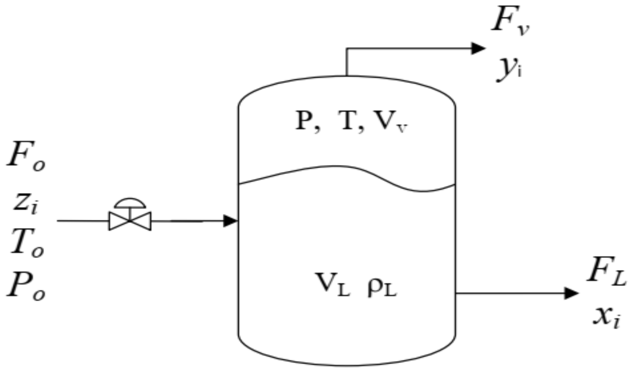

Figure 4.3 Multicomponent Flash Drum

For liquid phase:

Total mass balance:

$$\frac{d(\rho_L V_L)}{dt} = \rho_f F_f - \rho_L F_L - \rho_v F_v \tag{4.18}$$

Component balance:

$$\frac{d(\rho_L V_L x_i)}{dt} = \rho_f F_f z_i - \rho_L F_L x_i - \rho_v F_v y_i \quad (i=1,2,\ldots,N_c\text{-}1) \tag{4.19}$$

Energy balance:

$$\frac{d(\rho_L V_L \widetilde{h})}{dt} = \rho_f F_f \widetilde{h}_f - \rho_L F_L \widetilde{h} - \rho_v F_v \widetilde{H} \tag{4.20}$$

where $\widetilde{h}$ and $\widetilde{H}$ 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

$$y_i = \frac{x_i P_i^s}{P} \quad (i=1,2,\ldots.,N_c) \tag{4.21}$$

Together with the consistency relationships:

$$\sum_{i=1}^{Nc} y_i = 1 \tag{4.22}$$

$$\sum_{i=1}^{Nc} x_i = 1 \tag{4.23}$$

- Physical Properties:

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

$$\rho_L = f(x_i, T, P) \tag{4.24}$$

$$\rho_v = f(y_i, T, P) \approx M_v^{\text{ave}} P/R\,T \tag{4.25}$$

$$M_v^{\text{ave}} = \sum_{i=1}^{Nc} y_i M_i \tag{4.26}$$

$$h = f(x_i, T) \approx \sum_{i=1}^{Nc} x_i Cp_i (T - T_{ref}) \tag{4.27}$$

$$H = f(y_i, T) \approx \sum_{i=1}^{Nc} y_i Cp_i (T - T_{ref}) + \lambda_m \tag{4.28}$$

$$\lambda_m = \sum_{i=1}^{Nc} y_i \lambda_i \tag{4.29}$$

Degrees of freedom analysis:

- Forcing variables: F_f, T_f, P_f, z_i $(i=1,2..N_c)$,
- Remaining variables: $2N_c+5$: V_L, F_L, F_V, P, T, x_i $(i=1,2..N_c)$, $y_i(i=1,2,...N_c)$
- Number of equations: $2N_c+3$:

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.

4.3 REACTION WITH MASS TRANSFER

Figure 4.4 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:

$$A + B \rightarrow C \tag{4.30}$$

Assumptions:

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

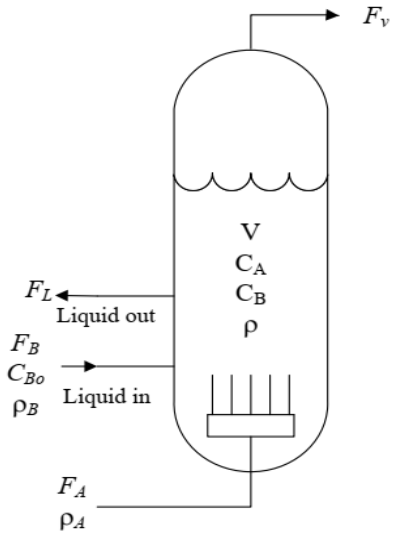

Figure 4.4 Reaction with Mass Transfer

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:

$$N_A = K_L\,(C^*_A - C_A) \tag{4.31}$$

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:

$$\frac{d\rho V}{dt} = \rho_B F_B + M_A A_m N_A - \rho F_L \tag{4.32}$$

Component balance on A:

$$V\frac{dC_A}{dt} = A_m N_A - F_L C_A - rV \tag{4.33}$$

Component balance on B:

$$V\frac{dC_B}{dt} = F_B C_{Bo} - F_L C_B - rV \tag{4.34}$$

Vapor phase:

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

$$F_v = F_A - M_A\, A_m\, N_A/\rho_A \tag{4.35}$$

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. 4.31- 4.36)

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.

4.4 BINARY ABSORPTION COLUMN

Consider a N stages binary absorption tower as shown in figure 4.5. 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:

$$y_i = a\,x_i + b \tag{4.36}$$

can be used for each stage i (i=1,2,…,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:

$$H\frac{dx_i}{dt} = G(y_{i-1} - y_i) + L(x_{i+1} - x_i) \quad \text{(i=2…,N-1)} \tag{4.37}$$

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:

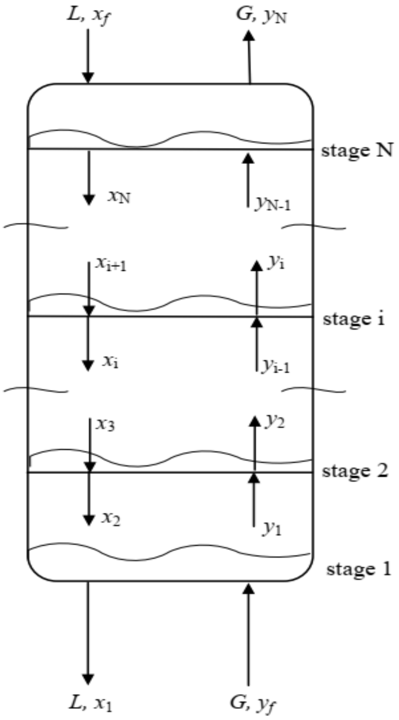

Figure 4.5 N-stages Absorbtion Tower

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…,N), y_i (i=1,2…,N)
- Number of equations:2N (Eqs4.37,4.38)

The problem is therefore is exactly specified.

4.5 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 rich in the light components and bottom product which is rich in the heavier components. A typical distillation column is shown in Figure 4.6. 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 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.

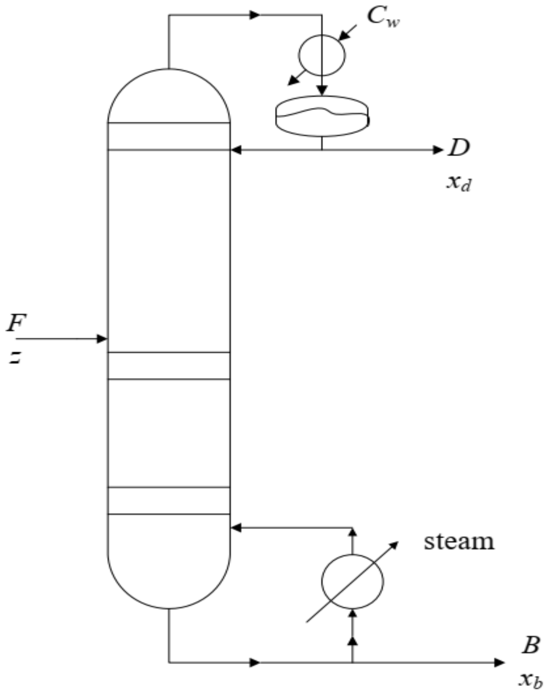

Figure 4.6 Distillation Column

Modeling the unit:

We are interested in developing the unsteady state model for the unit using the flowing 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 4.7a:

Total mass balance:

$$\frac{dM_D}{dt} = V_n - (R + D) \tag{4.38}$$

Component balance:

$$\frac{d(M_D x_{D,j})}{dt} = V_n y_{n,j} - (R + D)x_{D,j} \qquad j = 1, nc - 1 \tag{4.39}$$

Energy balance:

$$\frac{d(M_D h_D)}{dt} = V_n h_n - (R + D)h_D - Q_c \tag{4.40}$$

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

Stage n, Figure fig 4.7b

Total Mass balance:

Component balance:

$$\frac{d(M_f x_{f,j})}{dt} = V_{f-1} y_{f-1,j} - (V_f y_{f,j} + (1-q)Fz_j) + L_{f+1} x_{f+1,j} - (L_f x_{f,j} + qFz_j) \qquad j = 1, nc-1 \tag{4.48}$$

Energy balance:

$$\frac{d(M_f h_f)}{dt} = V_{f-1} H_{f-1} - (V_f H_f + (1-q)Fh_f) + L_{f+1} h_{f+1} - (L_f h_f + qFh_f) \tag{4.49}$$

Stage 1, Figure 4.7e

Total Mass balance:

$$\frac{dM_1}{dt} = V_B - V_1 + L_2 - L_1 \tag{4.50}$$

Component balance:

$$\frac{d(M_1 x_{1,j})}{dt} = V_B y_{B,j} - V_1 y_{1,j} + L_2 x_{2,j} - L_1 x_{1,j} \qquad j = 1, nc-1 \tag{4.51}$$

Energy balance:

$$\frac{d(M_1 h_1)}{dt} = V_B H_B - V_1 H_1 + L_2 h_2 - L_1 h_1 \tag{4.52}$$

Stage 0 (Re-boiler), Figure 4.7f

Total Mass balance:

$$\frac{dM_B}{dt} = -V_B + L_1 - B \tag{4.53}$$

Component balance:

$$\frac{dM_n}{dt} = V_{n-1} - V_n + R - L_n \tag{4.41}$$

Component balance:

$$\frac{d(M_n x_{n,j})}{dt} = V_{n-1} y_{n-1,j} - V_n y_{n,j} + R x_{D,j} - L_n x_{n,j} \qquad j = 1, nc-1 \tag{4.42}$$

Energy balance:

$$\frac{d(M_n h_n)}{dt} = V_{n-1} H_{n-1} - V_n H_n + R h_D - L_n h_n \tag{4.43}$$

Stage i, Figure 4.7c

Total Mass balance:

$$\frac{dM_i}{dt} = V_{i-1} - V_i + L_{i+1} - L_i \tag{4.44}$$

Component balance:

$$\frac{d(M_i x_{i,j})}{dt} = V_{i-1} y_{i-1,j} - V_i y_{i,j} + L_{i+1} x_{i+1,j} - L_i x_{i,j} \qquad j = 1, nc-1 \tag{4.45}$$

Energy balance:

$$\frac{d(M_i h_i)}{dt} = V_{i-1} H_{i-1} - V_i H_i + L_{i+1} h_{i+1} - L_i h_i \tag{4.46}$$

Stage f (Feed stage), Figure 4.7d

Total Mass balance:

$$\frac{dM_f}{dt} = V_{f-1} - (V_f + (1-q)F) + L_{f+1} - (L_f + qF) \tag{4.47}$$

$$\frac{d(M_B x_{B,j})}{dt} = -V_B y_{B,j} + L_1 x_{1,j} - B x_{B,j} \qquad j = 1, nc - 1 \tag{4.54}$$

Energy balance:

$$\frac{d(M_B h_B)}{dt} = -V_B H_B + L_1 h_1 - B h_B + Q_r \tag{4.55}$$

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
Total	$11+6n+2n(nc-1)+3(nc-1)$

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
$y_B = x_B$	$(nc-1)$
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 reboiler.
- Use V_B and R to control the end compositions i.e., x_B, x_D

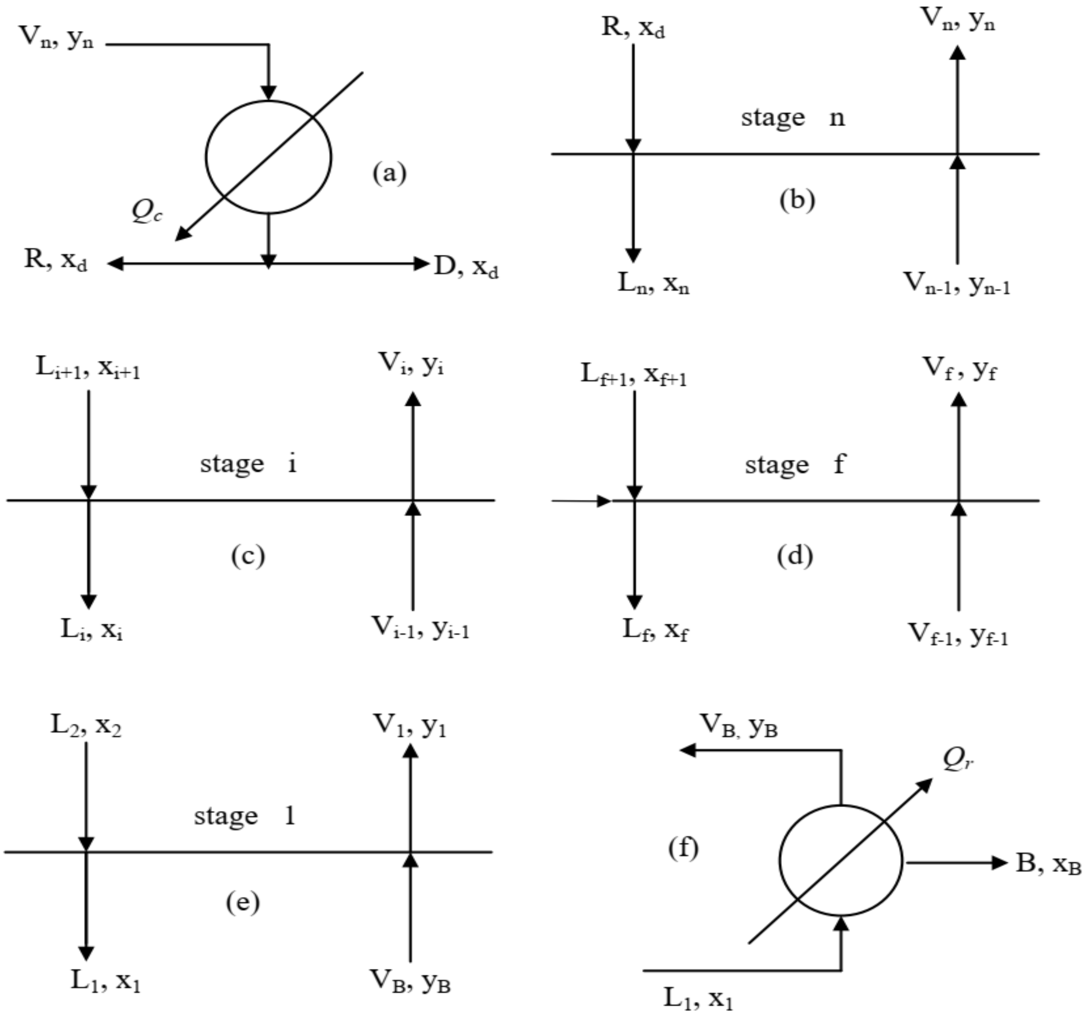

Figure 4.7 Distillation Column Stages

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:

$$V_B = V_1 = V_2 = \ldots = V_n \tag{4.56}$$

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

$$y_j = \alpha_j\, x_j/(1+(\alpha_j - 1)\, x_j) \tag{4.57}$$

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
Total	$2 + 2n + (2n + 3)(nc - 1)$

Equations:

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

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