

CHAPTER II

THEORY AND LITERATURE REVIEW

Since Marshall and Pigford (1947) first introduced a differential equation formulation of the dynamics of separation processes, several models of these processes have been proposed by Tolliver and Waggoner (1980). These models can be classified in two categories, high-order models and low-order models. The terms high-order model refers to dynamic models that are obtained by writing material and energy balances for each stage; they are usually highly nonlinear. This type of model can yield accurate representations of the physical process. On the other hand, low-order representations of separation processes are desirable for operator training, screening of control strategies, or use in on-line control schemes. Models of the low-order type are proposed either in transfer function or state-space form and are usually obtained by linearization and reduction of a model of the high-order type. They also may be obtained by postulating a transfer function form and then finding parameters through theoretical relationships or empirically, by fitting the response for a specific change in input.

In this chapter we briefly review both of high-order and low-order modeling methods for multicomponent distillation processes, underlining the need for low-order methods; then we utilize and develop a compartmental analysis. Furthermore, the thermodynamic properties' calculations have been included in this chapter because it needs to apply with the calculations.

2.1 Thermodynamic Properties Calculation

For multicomponent mixtures, thermodynamics properties cannot be use the graphical representations to determine equilibrium-stage requirements. Analytical computational procedures must be applied preferably by algebraic equations. Because mixture properties depend on temperature, pressure, and phase compositions, these equations tend to be complex. Nevertheless the equation presented in this chapter are widely used for computing phase equilibrium ratio (K -values and distribution coefficients), enthalpies and densities of mixtures over wide ranges of conditions using the equation of state, Soave-Redlich-Kwong equation (S-R-K).

2.1.1 Equation of state

Equipment design procedures for separation operations require phase enthalpies and densities in addition to phase equilibrium ratios. Classical thermodynamics provides a mean for obtaining all these quantities in a consistent manner from P - v - T relationships, which are usually referred to as equations of state. Although a large number of P - v - T equations have been proposed, relatively few are suitable for practical design calculations. Table 2.1 lists some of these. All the equations in Table 2.1 involve the universal gas constant R and, in all cases except two, other constants that are unique to a particular species. All equations of state can be applied to mixtures by means of mixing rules for combining pure species constants.

Equation (2-2) in Table 2.1, the ideal gas equation, is widely applied to pure gases and gas mixtures. This equation neglects molecular size and potential energy of molecular interactions. The mixture equation in terms of molal density ρ/M is:

$$\frac{\rho}{M} = \frac{1}{v} = \frac{P}{RT} = \frac{\sum_{i=1}^c n_i}{V} \quad (2-1)$$

Table 2.1 Equations of state

Name	Equation and Equation Number	Evaluation of Species Constants or Functions
Ideal gas law	$P = \frac{RT}{v} \quad (2-2)$	None
Generalised	$P = \frac{ZRT}{v} \quad (2-3)$	$Z = Z\{P_C, T_C, Z_C \text{ or } \omega\}$ as derived from experimental data
Virial (Onnes)	$P = \frac{RT}{v} \left(1 + \frac{B}{v} + \frac{C}{v^2} + \dots \right) \quad (2-4)$	From volumetric data, generalised correlations, or statistical mechanics, where B, C, and so on depend on temperature
van der Waals	$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2-5)$	$a = \frac{27 R^2 T_C^2}{64 P_C}, b = \frac{RT_C}{8 P_C}$
Beattie-Bridgeman	$P = \frac{RT}{v^2} \left(1 - \frac{c}{vT^3} \right) \left[v + B_0 \left(1 - \frac{b}{v} \right) \right] - \frac{A_0}{v^2} \left(1 - \frac{a}{v} \right) \quad (2-6)$	Constants a, A ₀ , b, B ₀ and c from experimental data
Benedict-Webb-Rubin (B-W-R)	$P = \frac{RT}{v} + \left[B_0 RT - A_0 - \frac{C_0}{T^2} \right] \frac{1}{v^2} + (bRT - a) \frac{1}{v^3} + \frac{a\alpha}{v^6} + \frac{c \left(1 + \frac{\gamma}{v^2} \right) \exp \left(-\frac{\gamma}{v^2} \right)}{v^3 T^2} \quad (2-7)$	Constants a, A ₀ , b, B ₀ , c, C ₀ , α, γ from experimental data or correlations
Redlich-Kwong	$P = \frac{RT}{v-b} - \frac{a}{T^{0.5} v(v+b)} \quad (2-8)$	$a = 0.4278 \frac{R^2 T_C^{2.5}}{P_C}, b = 0.0867 \frac{RT_C}{P_C}$

Source : Ernest J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, pp. 148, John Wiley & Sons Inc., New York, 1981.

The ideal gas law is generally accurate for pressures up to one atmosphere. At 50 psia (344.74 kPa), Equation (2-1) can exhibit deviations from experimental data as large as 10 %.

No corresponding simple equation of state exists for the liquid phase other than one based on the use of a known pure species liquid density and the assumptions of incompressibility and additive volumes. When a vapour is not an ideal gas, formulation of an accurate equation of state becomes difficult because of the necessity to account for molecular interactions. The principle of corresponding states, which is based on similitude of molecular behaviour particularly at the critical point, can be used to derive generalised graphical or tabular correlations of the vapour of liquid compressibility factor Z in (2-3) as a function of reduced (absolute) temperature $T_r = T / T_c$, reduced (absolute) pressure $P_r = P / P_c$, and a suitable third parameter. Generalised equations of state are often fitted to empirical equations in T_r and P_r for computerised design methods.

The virial equation of state in Table 2.1 provides a sound theoretical basis for computing P - v - T relationships of polar as well as nonpolar pure species and mixtures in the vapour phase. Virial coefficients B , C and higher can, in principle, be determined from statistical mechanics. However, the present state of development is such that most often (2-4) is truncated at B , the second virial coefficient, which is estimated from a generalised correlation. In this form, the virial equation is accurate to densities as high as approximately one half of critical.

The five-constant equation of Beattie and Bridgeman, the eight-constant equation of Benedict, Webb, and Rubin, B-W-R, (1940), and the two-constant equation of Redlich and Kwong, R-K, (1949), are empirical relationships applicable over a wide range of pressure. The R-K equation is particularly attractive because it contains only two constants and these can be determined directly from the critical temperature T_c and critical pressure P_c . Furthermore, the R-K equation has an

accuracy that compares quite favourably with more complex equations of state; and it has the ability to approximate the liquid region.

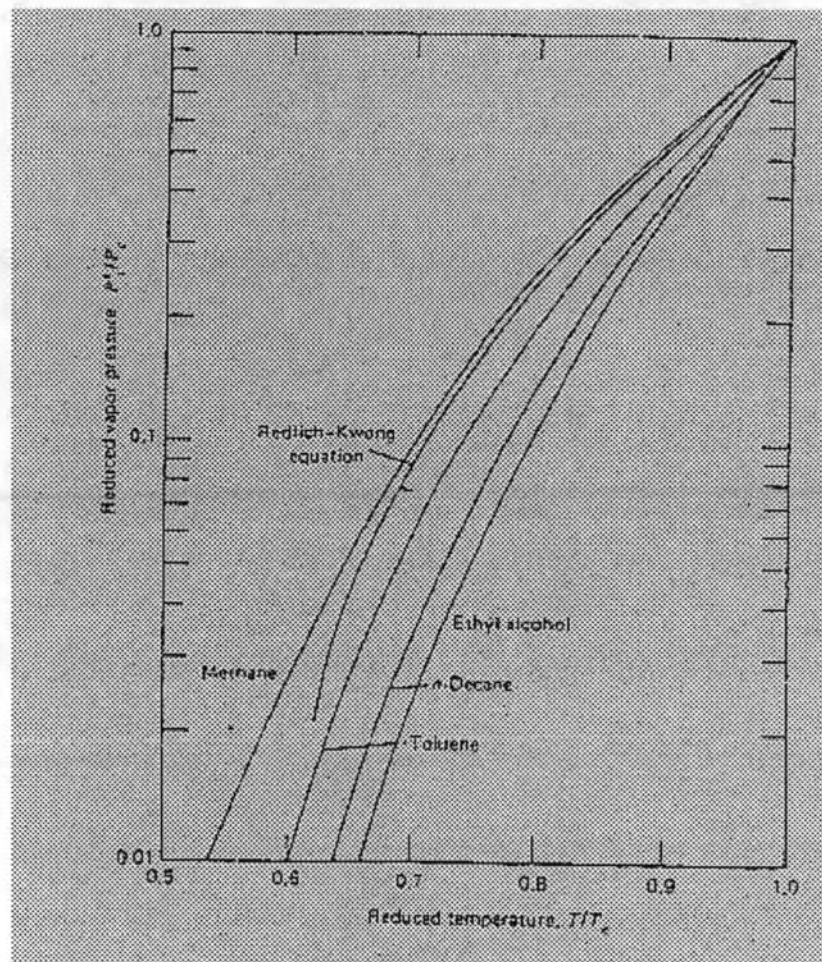


Figure 2.1 Reduced vapour pressure.

Source : Ernest J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, pp. 158, John Wiley & Sons Inc., New York, 1981.

However, the major difficulty with the original R-K equation is its failure to predict vapour pressure accurately, as was exhibited in Figure 2.1. Following the success of earlier work by Wilson (1966), Soave (1972) added a third parameter, the Pitzer acentric factor, to the R-K equation and obtained almost exact agreement with pure hydrocarbon vapour pressure data. The Soave modification of R-K equation, referred to here as the S-R-K equation, is

$$P = \frac{RT}{v-b} - \frac{2a}{v(v+b)} \quad (2-9)$$

Either (2-9) or the following equivalent compressibility factor forms are use when the S-R-K equation is applied to mixtures.

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (2-10)$$

where the mixing rules are

$$A = \frac{aP}{(RT)^2} \quad (2-11)$$

$$B = \frac{bP}{RT} \quad (2-12)$$

with

$$b = \sum_i^N x_i b_i \quad \text{or} \quad b = \sum_i^N y_i b_i \quad (2-13)$$

$$b_i = 0.08644 \frac{RT_{Ci}}{P_{Ci}} \quad (2-14)$$

$$a = \sum_i^N \sum_j^N x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

or

$$a = \sum_i^N \sum_j^N y_i y_j (a_i a_j)^{0.5} (1 - k_{ij})$$

(2-15)

$$a_i = a_{Ci} \alpha_i \quad (2-16)$$

$$a_{Ci} = 0.42748 \frac{(RT_{Ci})^2}{P_{Ci}} \quad (2-17)$$

$$\alpha_i^{0.5} = 1 + m_i (1 - T_r^{0.5}) \quad (2-18)$$

$$m_i = 0.48 + 1.574 \omega_i - 0.176 \omega_i^2 \quad (2-19)$$

Equation (2-10) is cubic equations in Z . Only one positive real root is obtained at supercritical temperatures where only a single phase exists. Otherwise, three real roots are obtained, the largest value of Z corresponding to a vapour phase, and the smallest value of Z to a liquid phase.

2.1.2 Thermodynamic Properties of Liquid and Vapour Phases

If ideal gas (zero pressure) specific heat or enthalpy equations for pure species are available, as well as an equation of state, thermodynamic properties can be derived in a consistent manner by applying the equations of classical thermodynamics compiled in Table 2.2. Equations (2-20) through (2-26) are applicable to vapour or liquid phases, where the superscript $^{\circ}$ refers to ideal gas.

2.1.2.1 Enthalpy

The molal specific heat of gases is conventionally given as a polynomial in temperature.

$$C_{PV}^{\circ} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (2-29)$$

Integration of (2-29) provides an equation for the ideal gas molal enthalpy at temperature T referred to a datum temperature T_0 .

$$H_V^{\circ} = \int_{T_0}^T C_{PV}^{\circ} dT = \sum_{k=1}^5 \frac{a_k (T^k - T_0^k)}{k} \quad (2-30)$$

Values of the five constants a_1 through a_5 , with T in $^{\circ}F$ and $T_0 = 0^{\circ}F$ are given in Appendix C for 176 compounds.

When the ideal gas law assumption is not valid, equation (2-20) is used to correct the enthalpy for pressure. For a pure species or mixtures at temperature T and pressure P , the vapour enthalpy is

$$H_V = \left[\sum_{i=1}^c (y_i H_{iV}^{\circ}) \right] + (H_V - H_V^{\circ}) \quad (2-31)$$

Equation (2-31) and (2-20) are particularly suitable for use with equations of state that are explicit in pressure (e.g., those shown in Table 2.1). The same two equations can be used to determine the liquid-phase enthalpy. Application is facilitated if the equation of state is continuous function in passing between vapour and liquid regions, as in Figure 2.2. Thus

$$H_L = \left[\sum_{i=1}^c (x_i H_{iV}^{\circ}) \right] + (H_L - H_V^{\circ}) \quad (2-32)$$

Table 2.2 Useful equations of classical thermodynamics**Integral equations**

$$(H - H_V^\circ) = Pv - RT - \int_{\infty}^v \left[P - T \left(\frac{\partial P}{\partial T} \right)_v \right] dv \quad (2-20)$$

$$v^\circ = \exp \left[\frac{1}{RT} \int_0^P \left(v - \frac{RT}{P} \right) dP \right] = \exp \left[\frac{1}{RT} \int_v^{\infty} \left(P - \frac{RT}{v} \right) dv - \ln Z + (Z - 1) \right] \quad (2-21)$$

$$\phi_i = \exp \left\{ \frac{1}{RT} \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln Z \right\} \quad (2-22)$$

where V is the total volume equal to $v \sum n_i$

Differential equations

$$(H_{iV}^\circ - H_i) = RT^2 \left(\frac{\partial \ln f_i}{\partial T} \right)_P \quad (2-23)$$

$$v_i = RT \left(\frac{\partial \ln f_i}{\partial P} \right)_T \quad (2-24)$$

$$(H_V^\circ - H) = RT^2 \left(\frac{\partial \ln v^\circ}{\partial T} \right)_P \quad (2-25)$$

$$v = RT \left[\left(\frac{\partial \ln v^\circ}{\partial P} \right)_T + \frac{1}{P} \right] \quad (2-26)$$

$$\left(\overline{H}_{iL} - H_{iL} \right) = \overline{H}_{iL}^E = -RT^2 \left(\frac{\partial \ln \gamma_{iL}}{\partial T} \right)_{P,x_i} \quad (2-27)$$

$$\left(\overline{v}_{iL} - v_{iL} \right) = \overline{v}_{iL}^E = RT \left(\frac{\partial \ln \gamma_{iL}}{\partial P} \right)_{T,x_i} \quad (2-28)$$

Source : Ernest J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, pp. 154, John Wiley & Sons Inc., New York, 1981.

For pure species at temperatures below critical, (2-32) can be divided into the separate contributions shown graphically in Figure 2.3 and analytically by (2-33), where the subscript s refers to saturation pressure conditions.

$$\begin{aligned}
 H_L = & \underbrace{H_V^\circ}_{(1) \text{ Vapor at Zero pressure}} + \underbrace{(P_v)_{V_s} - RT - \int_{\infty}^{v_{V_s}} \left[P - T \left(\frac{\partial P}{\partial T} \right)_v \right] dv}_{(2) \text{ Pressure correction for vapor to saturation pressure}} \\
 & \underbrace{-T \left(\frac{\partial P}{\partial T} \right)_s (v_{V_s} - v_{L_s})}_{(3) \text{ Latent heat of vaporization}} + \underbrace{(P_v)_L - (P_v)_{L_s} - \int_{v_{L_s}}^{v_L} \left[P - T \left(\frac{\partial P}{\partial T} \right)_v \right] dv}_{(4) \text{ Correction to liquid for pressure in excess of saturation pressure}} \quad (2-33)
 \end{aligned}$$

Equation (2-32) is preferred form, especially if the equation of state is a continuous function.

If the S-R-K equation of state is substituted into (2-20), the required integration is performed, and the result is substituted into (2-31) and (2-32), the equations for mixture molal enthalpy become

$$H_L = \sum_{i=1}^C (x_i H_{iV}^\circ) + RT \left\{ Z_L - 1 - \frac{A_L}{B_L} \left[1 - \frac{T}{a} \left(\frac{da}{dT} \right) \right] \ln \left(1 + \frac{B_L}{Z_L} \right) \right\} \quad (2-34)$$

$$H_V = \sum_{i=1}^C (y_i H_{iV}^\circ) + RT \left\{ Z_V - 1 - \frac{A_V}{B_V} \left[1 - \frac{T}{a} \left(\frac{da}{dT} \right) \right] \ln \left(1 + \frac{B_V}{Z_V} \right) \right\} \quad (2-35)$$

where

$$T \left(\frac{da}{dT} \right) = - \sum_i^N \sum_j^N x_i x_j m_j (a_i a_{C_i} T_{ij})^{0.5} (1 - k_{ij}) \quad (2-36)$$

or

$$T \left(\frac{da}{dT} \right) = - \sum_i^N \sum_j^N y_i y_j m_j (a_i a_{C_i} T_{ij})^{0.5} (1 - k_{ij}) \quad (2-37)$$

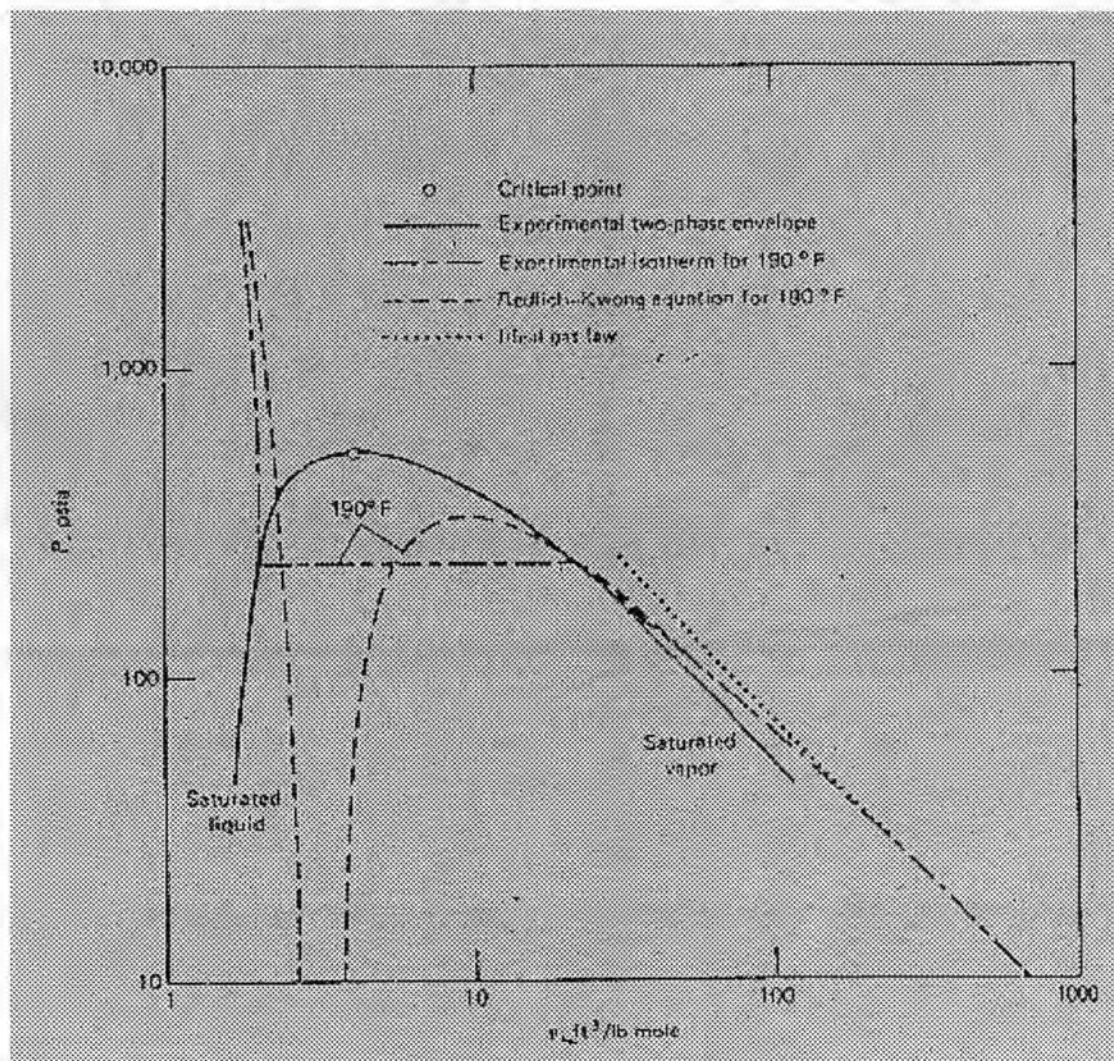


Figure 2.2 P - v - T properties of isobutane.

Source : Ernest J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, pp. 150, John Wiley & Sons Inc., New York, 1981.

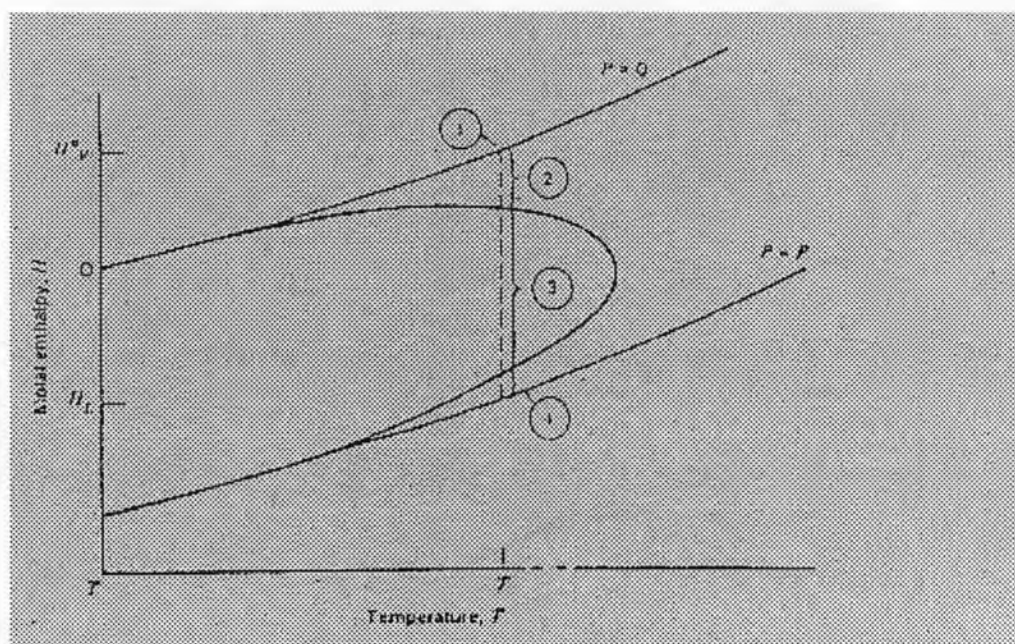


Figure 2.3 Contributions to enthalpy.

Source : Ernest J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, pp. 155, John Wiley & Sons Inc., New York, 1981.

2.1.2.2 Fugacity Coefficient

Fugacity coefficients of species in liquid or vapour mixtures can be obtained from (2-22). If the S-R-K equation of state is applied, a rather tedious procedure, as given by Soave-Redlich and Kwong, leads to the following working equations.

$$\phi_{iL} = \exp \left[(Z_L - 1)B'_i - \ln(Z_L - B_L) - \frac{A_L}{B_L}(A'_i - B'_i) \ln \left(1 + \frac{B_L}{Z_L} \right) \right] \quad (2-38)$$

$$\phi_{iV} = \exp \left[(Z_V - 1)B'_i - \ln(Z_V - B_V) - \frac{A_V}{B_V}(A'_i - B'_i) \ln \left(1 + \frac{B_V}{Z_V} \right) \right] \quad (2-39)$$

where

$$B'_i = \frac{b_i}{b} \quad (2-40)$$

$$A'_i = \frac{1}{a} \left[2a_i^{0.5} \sum_j^N x_j a_j^{0.5} (1 - k_{ij}) \right] \quad \text{or} \quad A'_i = \frac{1}{a} \left[2a_i^{0.5} \sum_j^N y_j a_j^{0.5} (1 - k_{ij}) \right] \quad (2-41)$$

2.1.2.3 Vapour-Liquid Equilibrium

Calculation of Vapour-Liquid Equilibrium (VLE) from an equation of state is based on the equilibrium equations.

$$y_i \phi_{iV} = x_i \phi_{iL} \quad (i = 1, 2, \dots, N) \quad (2-42)$$

Application of equation (2-42) requires the availability of a single P - v - T equation of state suitable for both liquid and vapour mixtures. The VLE relationships are invariably represented by

$$K_i = \frac{y_i}{x_i} = \frac{\phi_{iL}}{\phi_{iV}} \quad (i = 1, 2, \dots, N) \quad (2-43)$$

where the K_i are called equilibrium K -values. However, the resulting expressions for ϕ_i are generally complicated, and the calculations involve considerable iteration. They are therefore done with a computer. This can be shown the simplified block diagram for the VLE relationships as Figure 2.4.

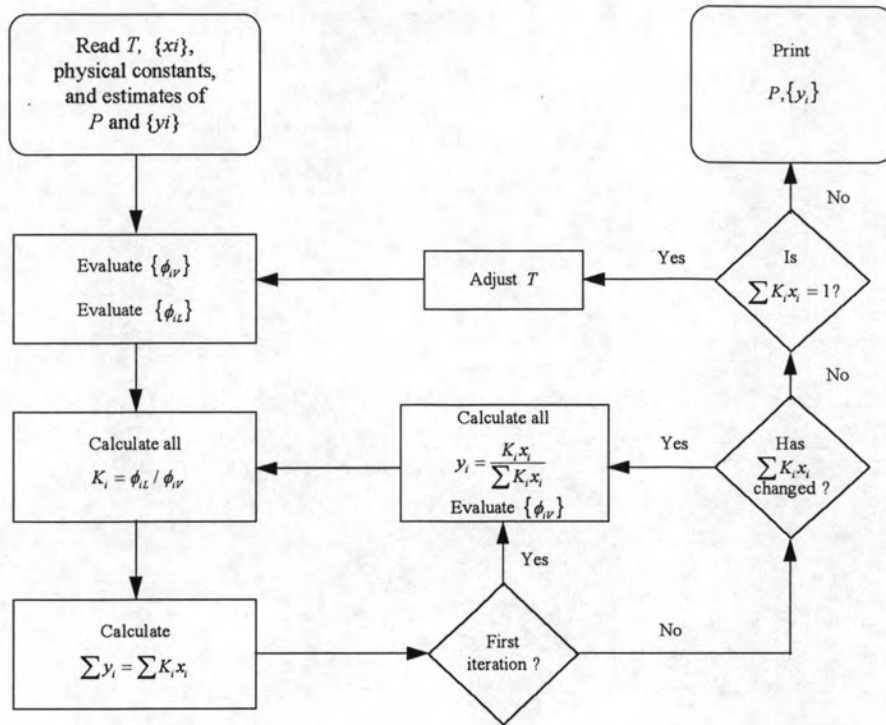


Figure 2.4 Block diagram for the calculation Bubble point.

Source : Hendrick C. Van Ness and Michael M. Abbott, Classical Thermodynamics of Nonelectrolyte Solutions With Applications to Phase Equilibria, pp. 284, McGraw-Hill Book Company, New York, 1982.

2.1.2.4 Density

By using the S-R-K equation of state (2-10), both compressibility factors of vapour and liquid are obtained and can be applied to find the mixture density as follows :

The molal volume is
$$v = \frac{ZRT}{P} \quad (2-44)$$

The density is the reciprocal of the specific volume.

$$\rho = \frac{1}{v/M} \quad (2-45)$$

where M is the molecular weight of the mixture.

2.2 High-order Modeling

It is well known that the stagewise calculation as rigorous method is required for final design of multicomponent distillation. This determination is made by solving material balance, energy (enthalpy) balance, and equilibrium relations for each stage. In this section, it will describe the mathematically of dynamic multicomponent distillation models. However, all thermodynamic properties are represented by using the S-R-K equation of state in previous section.

2.2.1 Steady state multicomponent distillation model

In principle, multicomponent equations are very similar to those for binary systems, but the solution involves substantially more computational effort. The model of distillation column is shown in Figure 2.5. For the sake of generality, it is shown that feed streams are introduced on every tray, and both liquid and vapour side streams are withdrawn from each tray. In an actual column, however, many of these values would be zero. Heat can be added or removed from each tray. Heat added is considered positive. The multicomponent mixture consists of C components. The feed to tray i is denoted by F_i and the liquid and vapour side streams are denoted by S_i^L and S_i^V , respectively. There are N equilibrium stages including a partial reboiler. Plates are numbered serially from the top. A partial condenser would constitute an

additional equilibrium stage. The trays are denoted by subscript i and the components by subscript j .

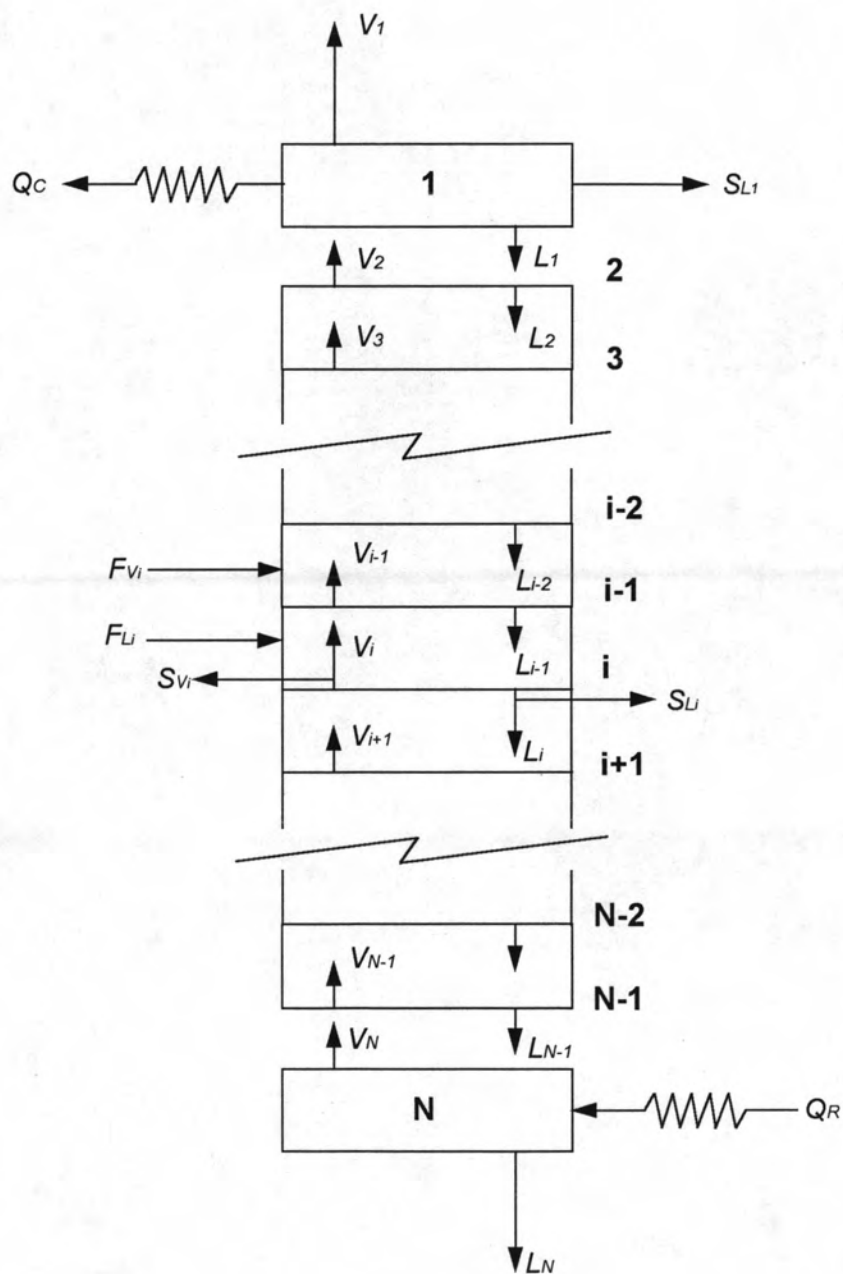


Figure 2.5 Schematic diagram of multicomponent distillation column

The basic equations describing the system are derived by taking material and energy balances around the tray i in the column. There are five sets of equations to describe the distillation operation :

- (a) overall material balances.
- (b) component material balances.
- (c) energy balances.
- (d) vapour-liquid equilibrium relationship.
- (e) component mole fraction summation equations.

Overall material balances :

$$V_{i+1} + \sum_{k=1}^i (F_k - S_k^V - S_k^L) - D - L_i = 0 \quad (i = 0, 1, 2, \dots, N) \quad (2-46)$$

Component material balance :

$$V_{i+1}y_{i+1,j} + L_{i-1}x_{i-1,j} + F_i z_{i,j} - (V_i + S_i^V)y_{i,j} - (L_i + S_i^L)x_{i,j} = 0$$

$$(i = 1, 2, \dots, N; j = 1, 2, \dots, C) \quad (2-47)$$

Heat balance :

$$V_{i+1}H_{i+1} + L_{i-1}h_{i-1} + F_i h_{Fi} - (V_i + S_i^V)H_i - (L_i + S_i^L)h_i + Q_i = 0$$

$$(i = 1, 2, \dots, N) \quad (2-48)$$

Vapour-Liquid equilibrium :

$$y_{i,j} - K_{i,j}x_{i,j} = 0 \quad (i = 1, 2, \dots, N; j = 1, 2, \dots, C) \quad (2-49)$$

Component summation equations :

$$\sum_{j=1}^C y_{i,j} - 1 = 0 \quad (i = 1, 2, \dots, N) \quad (2-50)$$

$$\sum_{j=1}^C x_{i,j} - 1 = 0 \quad (i = 1, 2, \dots, N) \quad (2-51)$$

Equations (2-50) and (2-51) can be combined to give

$$\sum_{j=1}^C y_{i,j} - \sum_{j=1}^C x_{i,j} = 0 \quad (i = 1, 2, \dots, N) \quad (2-52)$$

There are altogether $N(2C+3)$ equations. The unknowns are

internal vapour rates	N
internal liquid rates	N
tray temperatures	N
vapour mole fraction	CN
Liquid mole fraction	CN

Total $N(2C+3)$

2.2.2 Dynamic multicomponent distillation model

Basically dynamic models of multicomponent distillation are similar to the steady state model but the dynamic model would consider the accumulative term in each equation. The mathematics model of dynamic multicomponent distillation is

shown in Figure 2.6. The column contains a total of N_T theoretical trays. The liquid holdup on each tray including the downcomer is M_n (moles). The liquid is assumed to be perfectly mixed with a composition x_n . The holdup of vapour is assumed negligible throughout the system. Although the vapour volume is large, the number of moles is usually small because the vapour density is so much smaller than liquid density. This assumption breaks down, of course, in very high pressure columns. The liquid rates throughout the column will not be the same dynamically. They will depend on the fluid mechanics of the tray. Often simple Francis weir formula relationship, Equation 2-53, is used to relate the liquid holdup on a tray to the liquid flow rate L_n (moles/sec) over the outlet weir.

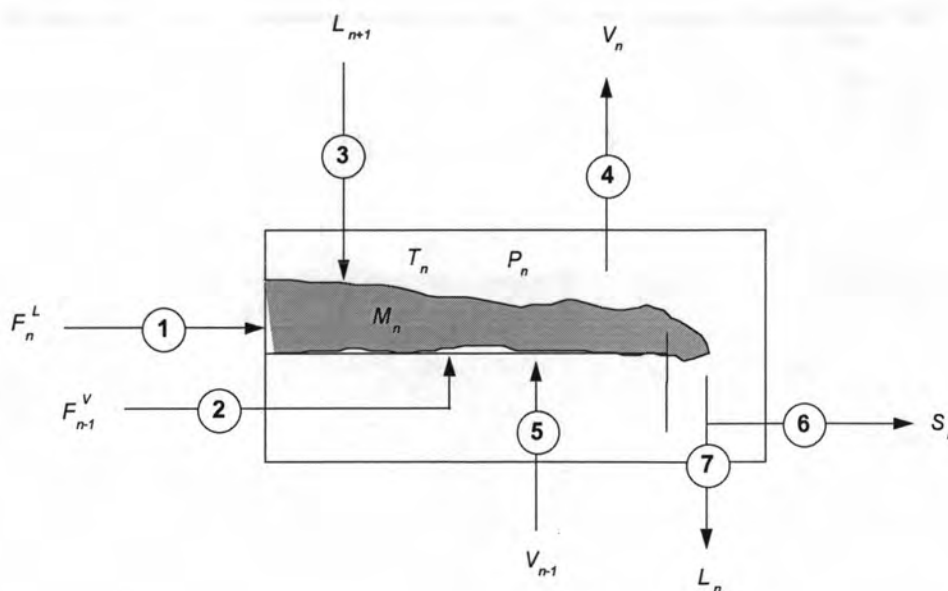


Figure 2.6 *n*th tray of multicomponent column.

Source : W. L. Luyben, Process Modeling Simulation, and Control for Chemical Engineering, pp. 76, McGraw-Hill Book Company, New York, 1974.

The Francis weir formula is

$$F_L = 3.33l(h)^{3/2} \quad (2-53)$$

where

$$F_L = \text{liquid rate, } ft^3 / \text{sec}$$

$$l = \text{length of weir, } ft$$

$$h = \text{height of liquid over weir, } ft$$

Total continuity equation (one per tray) :

$$\frac{dM_n}{dt} = L_{n+1} + F_n^L + F_{n-1}^V + V_{n-1} - V_n - L_n - S_n \quad (2-54)$$

Component continuity equation (J-1 per tray) :

$$\begin{aligned} \frac{d(M_n x_{nj})}{dt} = & L_{n+1} x_{n+1,j} + F_n^L x_{nj}^F + F_{n-1}^V y_{n-1,j}^F + V_{n-1} y_{n-1,j} \\ & - V_n y_{n-1,j} - L_n x_{nj} - S_n x_{nj} \end{aligned} \quad (2-55)$$

Energy (one per tray) :

$$\begin{aligned} \frac{d(M_n U_n)}{dt} = & L_{n+1} h_{n+1} + F_n^L h_n^F + F_{n-1}^V H_{n-1}^F + V_{n-1} H_{n-1} \\ & - V_n H_n - L_n h_n - S_n h_n \end{aligned} \quad (2-56)$$

where

$$U_n = \text{Internal energy, Btu/mole}$$

$$h = \text{Liquid Enthalpies, Btu/mole}$$

$$H = \text{Vapour Enthalpies, Btu/mole}$$

Phase equilibrium (J per tray) :

$$y_{nj}^* = f(x_{nj}, P_n, T_n) \quad (2-57)$$

Thermal properties :

$$\begin{aligned} h_n &= f(x_{nj}, T_n) \\ H_n &= f(y_{nj}, T_n, P_n) \\ h_n^F &= f(x_{nj}^F, T_n^F) \\ H_n^F &= f(y_{nj}^F, T_n^F, P_n) \end{aligned} \quad (2-58)$$

Equation of Motion :

$$\text{Liquid} \quad L_n = f(M_n, V_n, x_{nj}, T_n, P_n) \quad (2-59)$$

$$\text{Vapour} \quad V_n = f(P_n, P_{n-1}, y_{nj}, T_n) \quad (2-60)$$

Murphree vapour-phase equilibrium efficiency :

$$E_{nj} = \frac{y_{nj} - y_{n-1,j}^T}{y_{nj}^* - y_{n-1,j}^T} \quad (2-61)$$

where y_{nj}^* = composition of vapour in phase equilibrium with liquid on n th tray with composition x_n
 $y_{n-1,j}^T$ = actual vapour composition entering n th tray
 y_{nj} = actual vapour composition leaving n th tray
 E_{nj} = Murphree vapour efficiency for j th component on n th tray

2.3 Low-order Modeling

For a typical multicomponent process, a complete dynamic model may consist of several hundreds of differential equations, leading to computing times that make it impractical to use this type of model for on-line control. For the available models of low-order type, the hindrance lies in the fact that the model parameters often cannot be adjusted easily if process conditions change. Therefore, the reduced order techniques are mostly required.

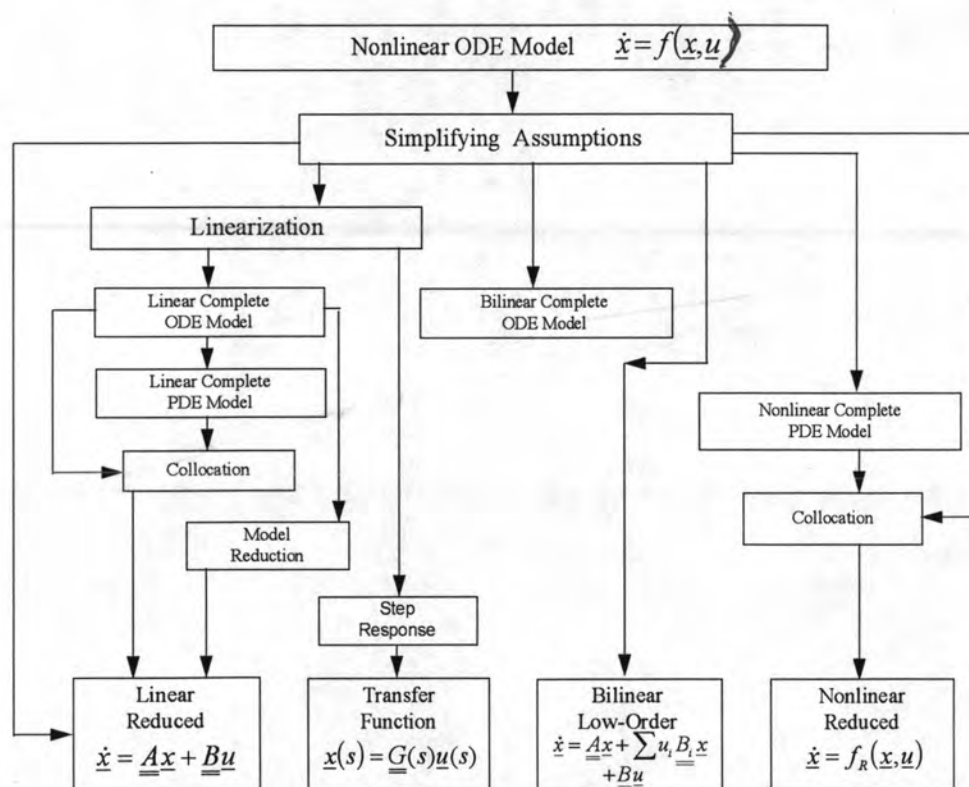


Figure 2.7 Available low-order modelling techniques.

Source : A. Benallou, D. E. Seborg, and D. A. Mellichamp, Dynamic Compartmental Models for Separation Process, pp. 1069, AICHE Journal, Vol 32, No. 7, July 1986.

2.3.1 Available Low-order Model

Figure 2.7 provides a summary of available low-order modelling techniques for distillation processes by Benallou, Seborg and Mellichamp(1986). These techniques can be classified according to the type of low-order models:

- (a) Linear low-order models
- (b) Bilinear low-order models
- (c) Nonlinear low-order models

Among methods of type (a), the most commonly used are those based on model reduction of a linear state-space model or on a transfer function approach that studied by Bonvin and Mellichamp (1982). In 1982 Georgakis and Stoeber used a compartmental approach to reduce the complete model. The method yields error bounds and utilizes physically meaningful variables in the reduced model. However, it also requires that a linearized, tridiagonal form of the complete model be developed; and it produces a linear, low-order model that does not match the original high-order model's steady states.

Another method of reducing the order of the system of linearized equations is based on the concept that the composition can be approximated as a continuous function of the distance along the column. Osborne et al (1965) used a "net mass transfer coefficient" for a column section to carry out the discretization or the method of orthogonal collocation. Wong and Luus (1980) proposed the latter technique to derive low-order lumped models. Orthogonal collocation can be used either directly on the linearized system equations or on partial differential equation formulation by Cho and Joseph (1980). Besides the mathematical complications introduced by orthogonal collocation (e.g., finding the roots of collocation polynomials for which a closed-form solution is possible only when their degree is not larger than 4, studied of Hermite (1905), interpolation, curve fitting of initial conditions), these models yield a set of fictitious state variables (compositions at the collocation points,

i.e., the roots of polynomials). Given that the collocation points seldom correspond to actual tray locations, the reduced-order model state variables must inevitably be interpolated in order to yield stage compositions. This difficulty leads to a common and important disadvantage of these methods: a discrepancy between the states of the reduced and complete models at steady state.

The third class of methods of type (a) leads to transfer function models. These models are usually obtained from a step, or an impulse response of the complete model or the process itself. Crockett (1978) reported that extensive investigation of physical interpretation of the parameters in these models has led to some empirical and theoretical relationships between the model parameters and process characteristics/operating condition. However, these relationships often are quite approximate and the empirical transfer function model form requires that an observer be used to eliminate internal state variables in the model for any on-line control applications.

In principle, type (b) or bilinear models provide a more accurate representation of the dynamic behaviour of distillation column than linear models since they retain the basic structure of the process; however, to our knowledge only one method of this type is discussed by Espana and Landau (1979). Unfortunately, the approach leads to a low-order model in which only one of three state variables, and none of the model parameters, has physical significance.

The last category, method (c), is used when a low-order, nonlinear representation of the process is sought. In one method, the reduction step is carried out by orthogonal collocation (Cho and Joseph). Consequently this approach inherits all of the collocation-introduced problems discussed earlier. An alternative compartmental approach for model reduction utilizes steady state material balance relationships for the individual stages to eliminate some of the stage compositions from the transient model, exactly as in steady state design methods. Such an approach thus

yields a nonlinear, low-order model that can match the steady states of original model. Dahlqvist (1979) used this approach to develop a low-order model of binary distillation column for adaptive control studies. He made no attempt to formalize the method nor to extend it more generally; nevertheless it does offer a number of conceptual advantages.

This reviews show that most of the available methods achieve model reduction by using some mathematical artifice that tends to blur the physical picture; consequently the physical significance of the resulting model parameters, and sometimes even the state variable, becomes lost and the relationship between the model and physical process becomes obscure. These observations led us to define a set of requirements that a low-order model designed for control purposes should possess:

- The model should retain the physical structure of the process.
- The state variables should have physical significance.
- The model parameters must be related to process parameters and should be easily obtainable from steady state plant data.

It is seen that none of the available low-order modeling methods satisfies all of these requirements with the possible exception of the compartmental approach that utilizes steady state stage relationships to eliminate superfluous concentration variables. In the next section this method is developed and elaborated to yield a general technique for the generation of distillation models that are inherently low-order and yet that retain the physical characteristics of the original processes.

2.3.2 Compartmental Modeling

In 1986 A. Benallou, D. E. Seborg, and D. A. Mellichamp presented a complete compartmental model for a binary distillation column. This modeling approach describes the dynamic operation of a staged process with significantly fewer

differential equations than is normally required for stage to stage models. The main assumption of the compartmental model is that several trays can be grouped into a single compartment and dynamically modeled as a single stage.

Using the compartmental concept, the column is considered to be made of a number of compartments (Figure 2.8), each compartment containing a number of stages. The different compartments are connected by liquid and vapour flows such that the vapour leaving the compartment is the same as the vapour leaving its first (top) stage, and the liquid leaving the compartment corresponds to the liquid from its last (bottom) stage. A typical compartment is shown in Figure 2.9. The basic idea in this compartmental approach is to associate the dynamic behaviour of a given compartment with that of one of its stages, the sensitive stage. The choice of the sensitive stage for a compartment can be based on physical considerations as discussed by Tolliver and McCune (1978) (e.g., the tray that most closely represents the average conditions prevailing within the entire compartment or that is most sensitive to external disturbances), or it may simply be dictated by instrumentation considerations (e.g., the tray for which a temperature or composition measurement is available, etc.). It is proposed to represent the dynamic behaviour of a compartment by that of a single stage whose inlet and outlet flows and composition match the flows and compositions of the compartment it represents, as in Figure 2.10. This representation is based on the following compartmentation assumption:

The dynamic behaviour of a section of stages, or a compartment, can be represented by that of a single stage having the same holdup as the total compartment holdup and the composition of the compartment sensitive stage.

Note that this assumption is considerably more general than that of Dahllqvist, who assumed that the entire compartment would be characterized by the concentration of the last (bottom) stage in the compartment.

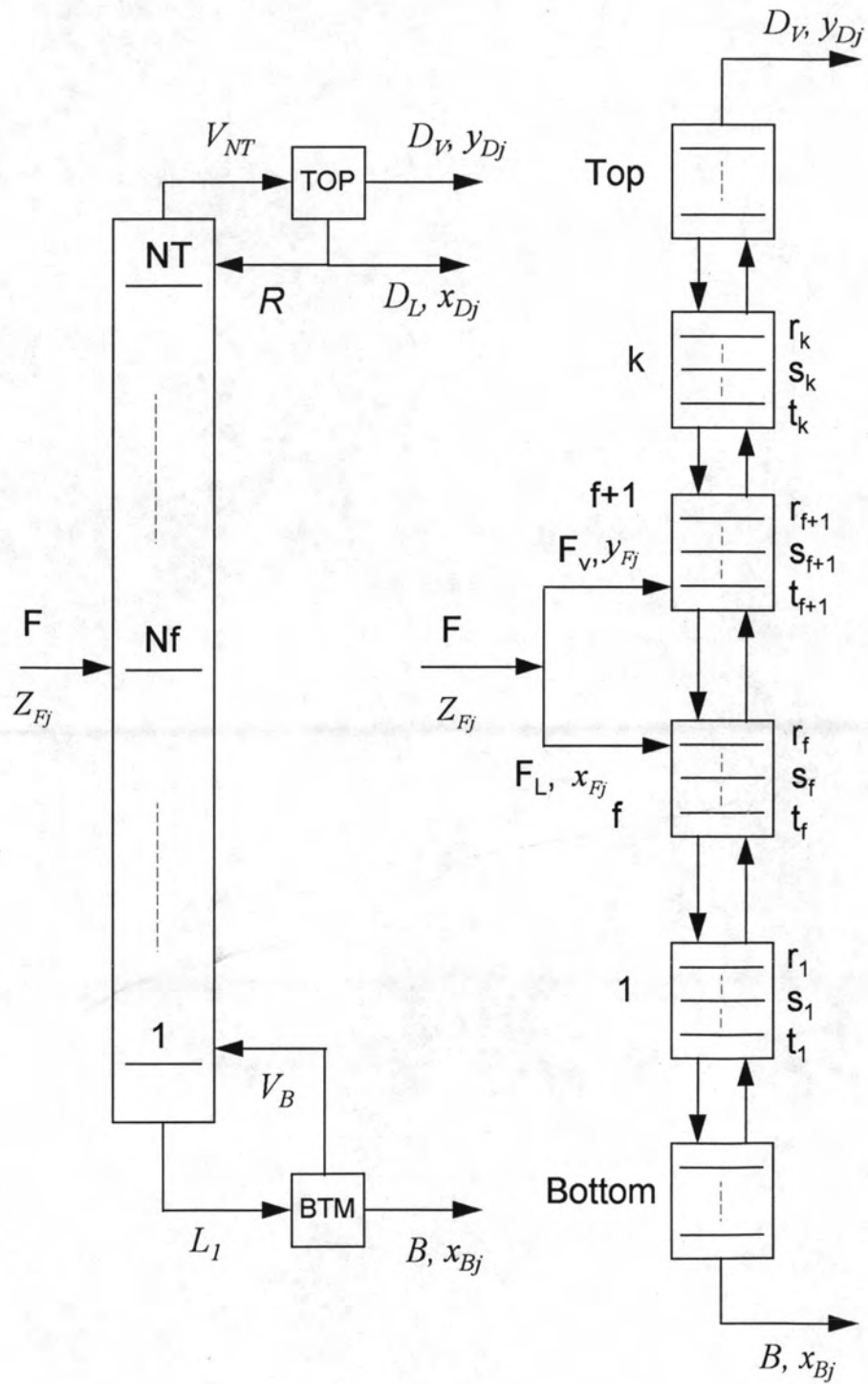


Figure 2.8 General compartmental representation of distillation column.

For a compartment containing stage r , the top stage in each compartment, through t , the bottom stage in each compartment, the total compartment holdup is given by:

$$M_C = \sum_{i=r}^t M_i \quad (2-62)$$

Using the compartmentation assumption, it is possible to represent the dynamic behaviour of a compartment by a single differential equation obtained from a dynamic material balance. The compartmental model then is the set of the dynamic equations obtained for all the compartments. In order to illustrate the development of the compartmental equations in more detail, it can be written a component balance for the compartment represented in Figure 2.9.

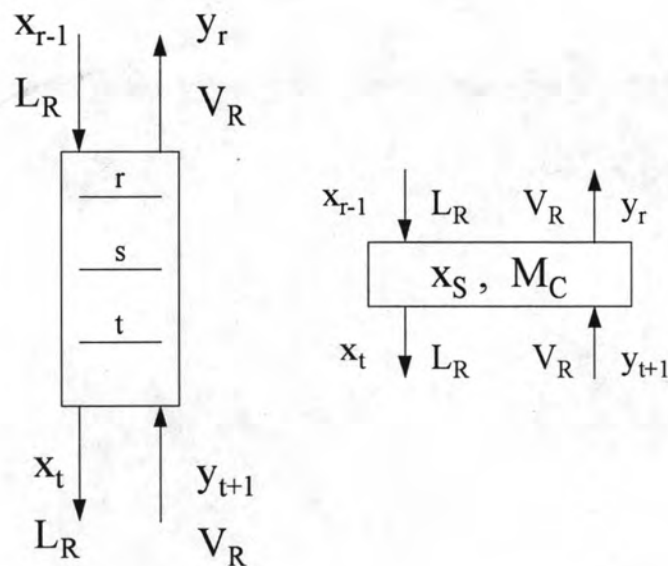


Figure 2.9 Sensitive stage representation of a compartment.

Using the compartmentation assumption, a material balance around the compartment yields:

$$M_c \frac{dx_s}{dt} = L_R x_{r-1} + V_R y_{t+1} - L_R x_t - V_R y_r \quad (2-63)$$

Next, approximate expressions for the compartment outlet streams, x_t and y_r will be derived in terms of the compartment sensitive stage composition, x_s , and the distillate composition, x_D or y_1 . These expressions are developed using shortcut calculation methods (Smoker, 1983; Garber and Lerman, 1943; Tiller and Tour, 1944; Edmister, 1957; Ramalho and Tiller, 1962) in such a way that the steady state material balances are preserved.

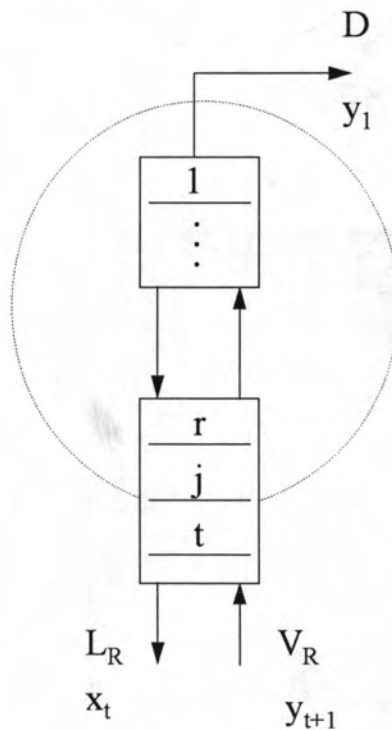


Figure 2.10 Material balance envelope for tray j .

Consider a steady state component balance around the envelope shown in Figure 2.10:

$$V_R y_{j+1} = L_R x_j + D y_1 \quad (2-64)$$

Assuming piecewise linear equilibrium,

$$y_j = K_j x_j, \quad j = 1, \dots, N \quad (2-65)$$

Equation (2-65) become:

$$L_R x_{j+1} = A_{j+1} (L_R x_j + D K_1 x_1) \quad (2-66)$$

where A_j is the absorption factor for stage j , defined by Edmister (1957):

$$A_j \equiv \frac{L_R}{V_R K_j} \quad \text{for } 2 \leq j \leq N_f \quad (2-67)$$

$$A_1 \equiv \frac{L_R}{D K_1} \quad (2-68)$$

Note that $D = V_R - L_R$ and $K_1 = 1$ for a total condenser.

Equation (2-66) is a first-order difference equation that can be solved easily by successive substitutions to yield the steady state solution for x_t in terms of the sensitive stage and first stage compositions:

$$L_R x_t = D K_1 x_1 (A_t + A_t A_{t-1} + \dots + A_t A_{t-1} \dots A_{s+1}) + A_t A_{t-1} \dots A_{s+1} \bullet L_R x_s \quad (2-69)$$

or

$$x_t = \left(\frac{V_R}{L_R} - 1 \right) K_1 x_1 \sum_s^t A + x_s \prod_s^t A \quad (2-70)$$

where $\sum_s^t A$ and $\prod_s^t A$ are extensions of the notation used by Edmister for the sums and products of the absorption factors. $\sum_s^t A$ and $\prod_s^t A$ are defined by:

$$\sum_s^t A = A_t + A_t A_{t-1} + \dots + A_t A_{t-1} \dots A_{s+1} \quad (2-71)$$

$$\prod_s^t A = A_t A_{t-1} \dots A_{s+1} \quad (2-72)$$

Equation (2-70) relates the steady state composition of the liquid leaving the compartment to the distillate and sensitive stage compositions. It is proposed to use the steady state relation as an approximate relation for transient conditions.

Using equation (2-70), it is defined the compartment separation function as the relationship between the composition of the liquid stream leaving the compartment, the terminal (distillate or bottoms) composition, and the sensitive tray composition:

$$g(x_1, x_s) = \left(\frac{V_R}{L_R} - 1 \right) K_1 x_1 \sum_s^t A + x_s \prod_s^t A \quad (2-73)$$

Similarly, the compartment separation function for the vapour stream leaving the compartment (stage r) is obtained from:

$$y_r = K_r \left[x_s - \left(\frac{V_R}{L_R} - 1 \right) K_1 x_1 \sum_r^s A \right] / \prod_r^s A \quad (2-74)$$

namely,

$$f(x_1, x_s) = K_r \left[x_s - \left(\frac{V_R}{L_R} - 1 \right) K_1 x_1 \sum_r^s A \right] / \prod_r^s A \quad (2-75)$$

Substitution of Equations (2-73) and (2-75) into Equation (2-63) yields the final model for the compartment:

$$M_C \frac{dx_s}{dt} = L_R x_{r-1} + V_R y_{t+1} - L_R g(x_1, x_s) - V_R f(x_1, x_s) \quad (2-76)$$

For the column represented in Figure 2.8, the compartmental model is obtained by writing Equation (2-76) for each compartment to obtained:

$$\begin{aligned} M_{Ci} \frac{dx_{si,j}}{d\tau} = & L_{i-1} g_{i-1,j}(x_{se,j}, x_{si-1,j}) + V_{i+1} f_{i+1,j}(x_{se,j}, x_{si,j}) \\ & - L_i g_{i,j}(x_{se,j}, x_{si,j}) - V_i f_{i,j}(x_{se,j}, x_{si,j}) \\ & + F_L x_{F,j} + F_V y_{F,j}; \quad 1 \leq i \leq k \end{aligned} \quad (2-77)$$

where f_i and g_i are generalizations of the compartment separations given by equation (2-73) and (2-75) for the first and last stages of compartment i :

$$\begin{aligned} f_{i,j}(x_{D,j}, x_{si,j}) = y_{ri,j} = & K_{ri,j} \left[x_{si,j} - \left(\frac{V_{NT}}{R + D_L} - 1 \right) K_{Dj} x_{D,j} \sum_{si}^{ri} A \right] / \prod_{si}^{ri} A; \\ & f + 1 \leq i \leq k \end{aligned} \quad (2-78)$$

$$\begin{aligned} f_{i,j}(x_{Bj}, x_{si,j}) = y_{ri,j} = & \left(\frac{L_1}{V_B} - 1 \right) x_{Bj} \sum_{si}^{ri} S + K_{si,j} x_{si,j} \prod_{si}^{ri} S \\ & 1 \leq i \leq f \end{aligned} \quad (2-79)$$

$$g_{i,j}(x_{D,j}, x_{si,j}) = x_{ti,j} = \left(\frac{V_{NT}}{R + D_L} - 1 \right) K_{D,j} x_{D,j} \sum_{ti}^{si} A + x_{si,j} \prod_{ti}^{si} A; \quad f+1 \leq i \leq k \quad (2-80)$$

$$g_{i,j}(x_{Nj}, x_{si,j}) = x_{ti,j} = \left[K_{si,j} x_{si,j} - \left(\frac{L_S}{V_S} - 1 \right) x_{N,j} \sum_{si}^{ti} S \right] / \left(K_{ti,j} \prod_{si}^{ti} S \right); \quad f+1 \leq i \leq k \quad (2-81)$$

where,

$$\sum_{si}^{ri} S = S_{si} + S_{si} S_{si+1} + \dots + S_{si} S_{si+1} \dots S_{ri} \quad (2-82)$$

$$\sum_{ti}^{si} S = S_{ti} + S_{ti} S_{ti+1} + \dots + S_{ti} S_{ti+1} \dots S_{si-1} \quad (2-83)$$

$$\prod_{si}^{ri} S = S_{si} S_{si+1} \dots S_{ri} \quad (2-84)$$

$$\prod_{ti}^{si} S = S_{ti} S_{ti+1} \dots S_{si-1} \quad (2-85)$$

$$S_{nj} = \frac{K_{nj} V_B}{L_1} \quad 1 \leq n \leq Nf - 1 \quad (2-86)$$

$$B = L_1 - V_B \quad (2-87)$$

$$\sum_{si}^{ri} A = A_{si} + A_{si} A_{si+1} + \dots + A_{si} A_{si+1} \dots A_{ri} \quad (2-88)$$

$$\sum_{ti}^{si} A = A_{ti} + A_{ti} A_{ti+1} + \dots + A_{ti} A_{ti+1} \dots A_{si-1} \quad (2-89)$$

$$\prod_{si}^{ri} A = A_{si} A_{si+1} \dots A_{ri} \quad (2-90)$$

$$\prod_{ti}^{si} A = A_{ti} A_{ti+1} \dots A_{si-1} \quad (2-91)$$

$$A_j \equiv \frac{R + D_L}{V_{NT} K_j} \quad \text{for } Nf \leq j \leq NT \quad (2-92)$$

$$D_V = V_{NT} - D_L - R \quad (2-93)$$

The subscript *se* denotes the appropriate terminal concentration.

$$se = s1 = D, \text{ for the rectification compartments} \quad (2-94)$$

$$se = sk = B, \text{ for the stripping compartments} \quad (2-95)$$

Also,

$$\begin{aligned} L_0 &= 0 \\ L_i &= L_1 \quad \text{for } 1 \leq i \leq f - 1 \\ L_i &= R + D_L \quad \text{for } f \leq i \leq k \end{aligned} \quad (2-96)$$

$$\begin{aligned} V_i &= V_B \quad \text{for } 1 \leq i \leq f - 1 \\ V_i &= V_{NT} \quad \text{for } f \leq i \leq k \end{aligned} \quad (2-97)$$

Remark

1. Equations (2-77) through (2-97) represent a compartmental model for a simple multicomponent distillation where the retained stage concentrations (state

variables) and the compartmental configuration can be chosen independently and arbitrarily.

2. The order of the compartmental model is k , the number of compartments, which will normally be much less than NT , the number of total plates in the column. The compartmental model also includes the four algebraic equations consisting of the compartment separation functions in Equations (2-78) through (2-81). Notice that these functions are expressed analytically in terms of the process parameters. This type of formulation is particularly useful if the process conditions change since the same model is still valid.

3. In contrast to existing low-order modeling techniques, use of compartmental analysis does not require that the complete high-order model be available. Rather, the low-order material balances are written out directly using compartmental functions.

4. In the model given by equations (2-77) through (2-97), it has been imposed the condition that the sensitive stages of first and last compartments be the condenser and reboiler stages, respectively. This assumption is not necessary, but it permits the top and bottom compositions to be retained as state variables.

5. Because of the nature of the compartment separation functions, steady state agreement between the complete and compartmental models will be guaranteed, i.e., the compartmental model will predict the correct steady state for an arbitrary change in any of the input variables. In fact, at steady state, the compartmental model is identical to the complete model in which the "non-sensitive" compositions and their corresponding equations are eliminated using shortcut expressions. No more than two compartments are required to obtain an approximate dynamic model that matches distillate and bottoms compositions exactly. Among the available low-order modeling techniques, steady state agreement can be achieved only in the linear case (Marshall, 1966; Litz, 1981). For nonlinear models with constant

relative volatility, some of the methods based on orthogonal collocation yield models that satisfy material balances; however these methods do not guarantee steady state agreement between the collocation and complete models.

2.3.3 Guidelines for Compartmental modeling

As a guideline for selecting sensitive trays within a compartment, Benallou et al (1986) has suggested using Tolliver and McCuun's (1978) approach, while Bequette and Edgar (1989), among others, have used the singular value decomposition technique to select tray locations. Benallou et al have been selected the condenser and reboiler stages as the first and last sensitive tray respectively. For the feed compartment, the sensitive tray was taken at the feed location; for the remaining compartments, sensitive trays were taken midway between the first and last stages in the compartment.

In 1990 R. R. Horton, B. W. Bequette, and T. F. Edgar found that sensitive tray selection within a compartment has an only slight effect on response accuracy. However, the sensitive tray selection has a significant effect on computational times. Therefore, he proposed another guideline for compartmental model as follows:

1. The stripping section should have sensitive stages in the lower portion of each compartment, approximately three-quarters of the way down.
2. The rectifying section should have sensitive stages in the upper portion of each compartment, approximately one-quarter of the way down.
3. The reboiler and condenser should be chosen as sensitive stages in their compartments but do not need to be isolated in individual compartments.
4. The column should be divided at a point several trays below the feed tray for algebraic (steady state material balance) computation of non-sensitive stage compositions.