

CHAPTER 1

FUNDAMENTALS OF VAPOR–LIQUID PHASE EQUILIBRIUM (VLE)

Distillation occupies a very important position in chemical engineering. Distillation and chemical reactors represent the backbone of what distinguishes chemical engineering from other engineering disciplines. Operations involving heat transfer and fluid mechanics are common to several disciplines. But distillation is uniquely under the purview of chemical engineers.

The basis of distillation is phase equilibrium, specifically, vapor–liquid (phase) equilibrium (VLE) and in some cases vapor–liquid–liquid (phase) equilibrium (VLLE). Distillation can effect a separation among chemical components only if the compositions of the vapor and liquid phases that are in phase equilibrium with each other are different. A reasonable understanding of VLE is essential for the analysis, design, and control of distillation columns.

The fundamentals of VLE are briefly reviewed in this chapter.

1.1 VAPOR PRESSURE

Vapor pressure is a physical property of a pure chemical component. It is the pressure that a pure component exerts at a given temperature when both liquid and vapor phases are present. Laboratory vapor pressure data, usually generated by chemists, are available for most of the chemical components of importance in industry.

Vapor pressure depends **only** on temperature. It does not depend on composition because it is a pure component property. This dependence is normally a strong one with an exponential increase in vapor pressure with increasing temperature. Figure 1.1 gives two typical vapor pressure curves, one for benzene and one for toluene. The natural log of the vapor pressures of the two components are plotted against the reciprocal of the

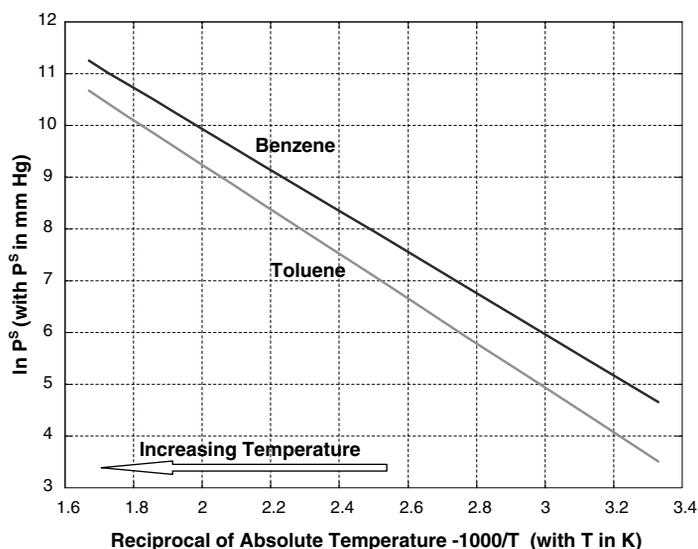


Figure 1.1 Vapor pressures of pure benzene and toluene.

absolute temperature. As temperature increases, we move to the left in the figure, which means a higher vapor pressure. In this particular figure, the vapor pressure P^S of each component is given in units of millimeters of mercury (mmHg). The temperature is given in Kelvin units.

Looking at a vertical constant-temperature line shows that benzene has a higher vapor pressure than does toluene at a given temperature. Therefore benzene is the “lighter” component from the standpoint of volatility (not density). Looking at a constant-pressure horizontal line shows that benzene boils at a lower temperature than does toluene. Therefore benzene is the “lower boiling” component. Note that the vapor pressure lines for benzene and toluene are fairly parallel. This means that the ratio of the vapor pressures does not change much with temperature (or pressure). As discussed in a later section, this means that the ease or difficulty of the benzene/toluene separation (the energy required to make a specified separation) does not change much with the operating pressure of the column. Other chemical components can have temperature dependences that are quite different.

If we have a vessel containing a mixture of these two components with liquid and vapor phases present, the concentration of benzene in the vapor phase will be higher than that in the liquid phase. The reverse is true for the heavier, higher-boiling toluene. Therefore benzene and toluene can be separated in a distillation column into an overhead distillate stream that is fairly pure benzene and a bottoms stream that is fairly pure toluene.

Equations can be fitted to the experimental vapor pressure data for each component using two, three, or more parameters. For example, the two-parameter version is

$$\ln P_j^S = C_j + D_j/T$$

The C_j and D_j are constants for each pure chemical component. Their numerical values depend on the units used for vapor pressure [mmHg, kPa, psia (pounds per square inch absolute), atm, etc.] and on the units used for temperature (K or °R).

1.2 BINARY VLE PHASE DIAGRAMS

Two types of vapor–liquid equilibrium diagrams are widely used to represent data for two-component (binary) systems. The first is a “temperature versus x and y ” diagram (Txy). The x term represents the liquid composition, usually expressed in terms of mole fraction. The y term represents the vapor composition. The second diagram is a plot of x versus y .

These types of diagrams are generated at a constant pressure. Since the pressure in a distillation column is relatively constant in most columns (the exception is vacuum distillation, in which the pressures at the top and bottom are significantly different in terms of absolute pressure level), a Txy diagram, and an xy diagram are convenient for the analysis of binary distillation systems.

Figure 1.2 gives the Txy diagram for the benzene/toluene system at a pressure of 1 atm. The abscissa shows the mole fraction of benzene; the ordinate, temperature. The lower curve is the “saturated liquid” line, which gives the mole fraction of benzene in the liquid phase x . The upper curve is the “saturated vapor” line, which gives the mole fraction of benzene in the vapor phase y . Drawing a horizontal line at some temperature and reading off the intersection of this line with the two curves give the compositions of the two phases. For example, at 370 K the value of x is 0.375 mole fraction benzene and the value of y is 0.586 mole fraction benzene. As expected, the vapor is richer in the lighter component.

At the leftmost point we have pure toluene (0 mole fraction benzene), so the boiling point of toluene at 1 atm can be read from the diagram (384.7 K). At the rightmost point we have pure benzene (1 mole fraction benzene), so the boiling point of benzene at 1 atm can be read from the diagram (353.0 K). In the region between the curves, there are two phases; in the region above the saturated vapor curve, there is only a single “superheated” vapor phase; in the region below the saturated liquid curve, there is only a single “subcooled” liquid phase.

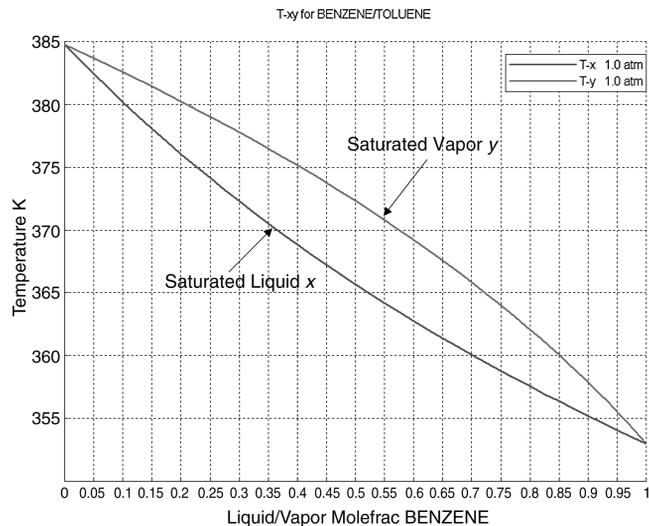


Figure 1.2 Txy diagram for benzene and toluene at 1 atm.

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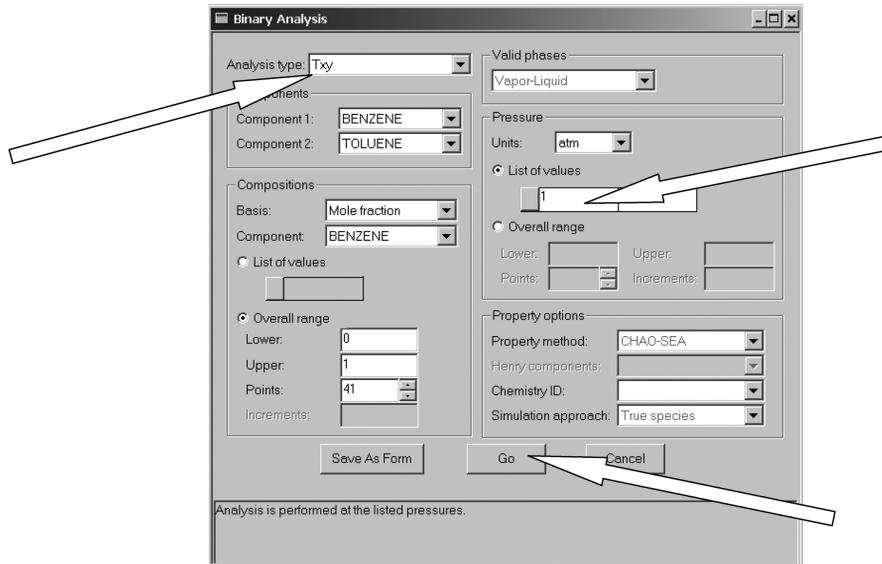


Figure 1.3 Specifying Txy diagram parameters.

The diagram is easily generated in Aspen Plus by going to *Tools* on the upper toolbar and selecting *Analysis, Property, and Binary*. The window shown in Figure 1.3 opens and specifies the type of diagram and the pressure. Then we click the *Go* button.

The pressure in the Txy diagram given in Figure 1.2 is 1 atm. Results at several pressures can also be generated as illustrated in Figure 1.4. The higher the pressure, the higher the temperatures.

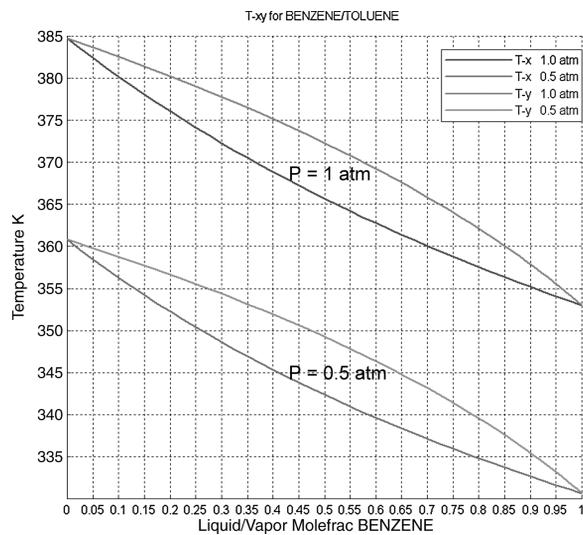


Figure 1.4 Txy diagrams at two pressures.

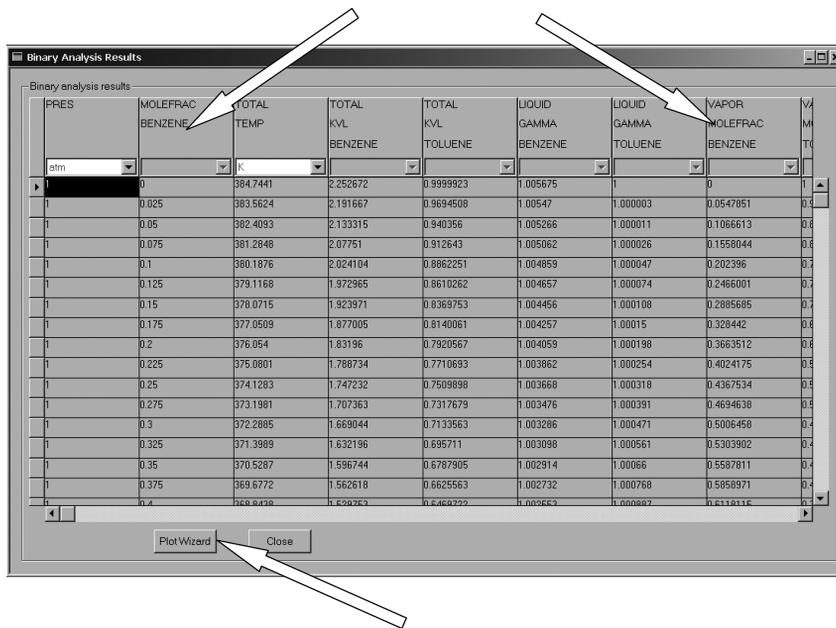


Figure 1.5 Using Plot Wizard to generate xy diagram.

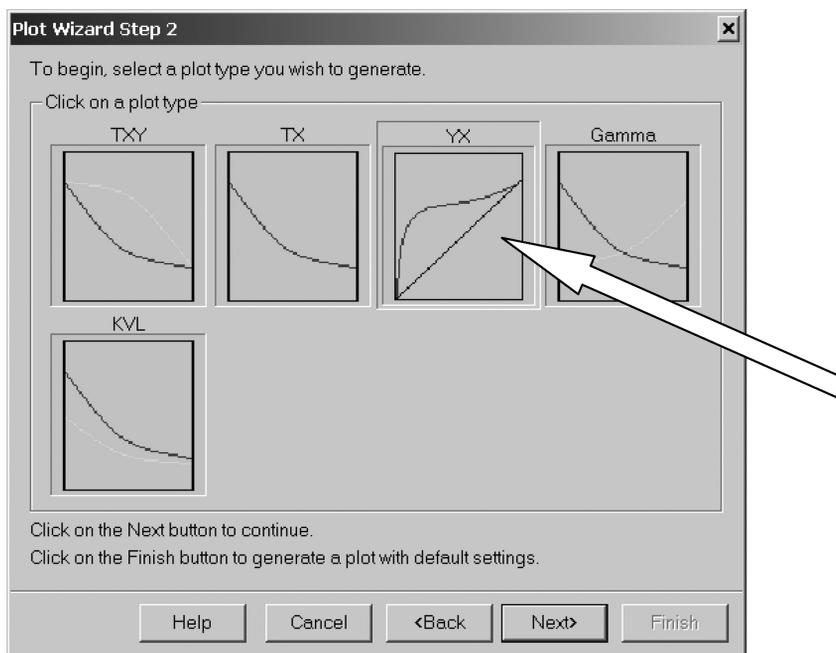


Figure 1.6 Using Plot Wizard to generate xy diagram.

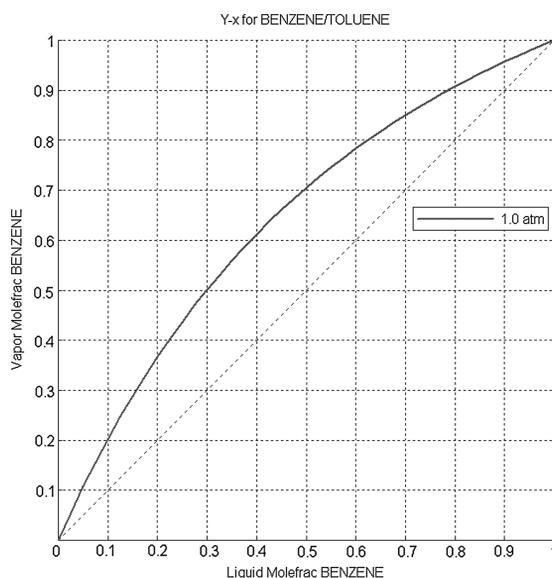


Figure 1.7 xy diagram for benzene/toluene.

The other type of diagram, an xy diagram, is generated in Aspen Plus by clicking the *Plot Wizard* button at the bottom of the *Binary Analysis Results* window that also opens when the *Go* button is clicked to generate the Txy diagram. As shown in Figure 1.5, this window also gives a table of detailed information. The window shown in Figure 1.6 opens, and YX picture is selected. Clicking the *Next* and *Finish* buttons generates the xy diagram shown in Figure 1.7.

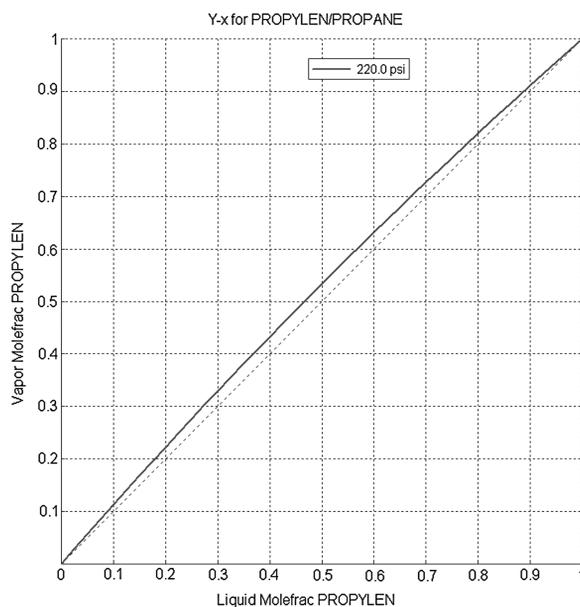


Figure 1.8 xy diagram for propylene/propane.

Figure 1.8 gives an xy diagram for the propylene/propane system. These components have boiling points that are quite close, which leads to a very difficult separation.

These diagrams provide valuable insight into the VLE of binary systems. They can be used for quantitative analysis of distillation columns, as we will demonstrate in Chapter 2. Three-component ternary systems can also be represented graphically, as discussed in Section 1.6.

1.3 PHYSICAL PROPERTY METHODS

The observant reader may have noticed in Figure 1.3 that the physical property method specified for the VLE calculations in the benzene/toluene example was “Chao–Seader.” This method works well for most hydrocarbon systems.

One of the most important issues involved in distillation calculations is the selection of an appropriate physical property method that will accurately describe the phase equilibrium of the chemical component system. The Aspen Plus library has a large number of alternative methods. Some of the most commonly used methods are Chao–Seader, van Laar, Wilson, Unifac, and NRTL.

In most design situations there is some type of data that can be used to select the most appropriate physical property method. Often VLE data can be found in the literature. The multivolume DECHEMA data books¹ provide an extensive source of data.

If operating data from a laboratory, pilot plant, or plant column are available, they can be used to determine what physical property method fits the column data. There could be a problem in using column data in that the tray efficiency is also unknown and the VLE parameters cannot be decoupled from the efficiency.

1.4 RELATIVE VOLATILITY

One of the most useful ways to represent VLE data is by employing “relative volatility,” which is the ratio of the y/x values [vapor mole fraction over (divided by) liquid mole fraction] of two components. For example, the relative volatility of component L with respect to component H is defined in the following equation:

$$\alpha_{LH} \equiv \frac{y_L/x_L}{y_H/x_H}$$

The larger the relative volatility, the easier the separation.

Relative volatilities can be applied to both binary and multicomponent systems. In the binary case, the relative volatility α between the light and heavy components can be used to give a simple relationship between the composition of the liquid phase (x is the mole fraction of the light component in the liquid phase) and the composition of the vapor phase (y is the mole fraction of the light component in the vapor phase):

$$y = \frac{\alpha x}{1 + (\alpha - 1)x}$$

¹J. Gmehling et al., *Vapor-Liquid Equilibrium Data Collection*, DECHEMA, Frankfurt/Main, 1993.

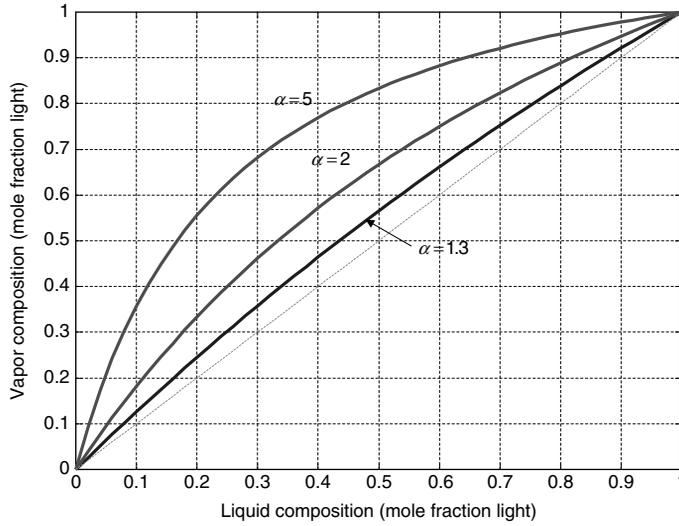


Figure 1.9 xy curves for relative volatilities of 1.3, 2, and 5.

Figure 1.9 gives xy curves for several values of α , assuming that α is constant over the entire composition space.

In the multicomponent case, a similar relationship can be derived. Suppose that there are NC components. Component 1 is the lightest, component 2 is the next lightest, and so forth down to the heaviest of all the components, component H . We define the relative volatility of component j with respect to component H as α_j :

$$\alpha_j = \frac{y_j/x_j}{y_H/x_H}$$

Solving for y_j and summing all the y values (which must add to unity) give

$$y_j = \alpha_j x_j \frac{y_H}{x_H}$$

$$\sum_{j=1}^{NC} y_j = 1 = \sum_{j=1}^{NC} \alpha_j x_j \frac{y_H}{x_H}$$

$$1 = \frac{y_H}{x_H} \sum_{j=1}^{NC} \alpha_j x_j$$

Then, solving for y_H/x_H and substituting this into the first equation above give

$$\frac{y_H}{x_H} = \frac{1}{\sum_{j=1}^{NC} \alpha_j x_j}$$

$$y_j = \frac{\alpha_j x_j}{\sum_{j=1}^{NC} \alpha_j x_j}$$

The last equation relates the vapor composition to the liquid composition for a constant relative volatility multicomponent system. Of course, if relative volatilities are not constant, this equation cannot be used. What is required is a “bubblepoint” calculation, which is discussed in the next section.

1.5 BUBBLEPOINT CALCULATIONS

The most common VLE problem is to calculate the temperature and vapor composition y_j that is in equilibrium with a liquid at a known total pressure of the system P and with a known liquid composition (all the x_j values). At phase equilibrium the “chemical potential” μ_j of each component in the liquid and vapor phases must be equal:

$$\mu_j^L = \mu_j^V$$

The liquid-phase chemical potential of component j can be expressed in terms of liquid mole fraction x_j , vapor pressure P_j^S , and activity coefficient γ_j :

$$\mu_j^L = x_j P_j^S \gamma_j$$

The vapor-phase chemical potential of component j can be expressed in terms of vapor mole fraction y_j , the total system pressure P , and fugacity coefficient σ_j :

$$\mu_j^V = y_j P \sigma_j$$

Therefore the general relationship between vapor and liquid phases is

$$y_j P \sigma_j = x_j P_j^S \gamma_j$$

If the pressure of the system is not high, the fugacity coefficient is unity. If the liquid phase is “ideal” (i.e., there is no interaction between the molecules), the activity coefficient is unity. The latter situation is much less common than the former because components interact in liquid mixtures. They can either attract or repulse. Section 1.7 discusses nonideal systems in more detail.

Let us assume that the liquid and vapor phases are both ideal ($\gamma_j = 1$ and $\sigma_j = 1$). In this situation the bubblepoint calculation involves an iterative calculation to find the temperature T that satisfies the equation

$$P = \sum_{j=1}^{NC} x_j P_{j(T)}^S$$

The total pressure P and all the x_j values are known. In addition, equations for the vapor pressures of all components as functions of temperature T are known. The Newton–Raphson convergence method is convenient and efficient in this iterative calculation because an analytical derivative of the temperature-dependent vapor pressure functions P_j^S can be used.

1.6 TERNARY DIAGRAMS

Three-component systems can be represented in two-dimensional ternary diagrams. There are three components, but the sum of the mole fractions must add to unity. Therefore, specifying two mole fractions completely defines the composition.

A typical rectangular ternary diagram is given in Figure 1.10. The mole fraction of component 1 is shown on the abscissa; the mole fraction of component 2, on the ordinate. Both of these dimensions run from 0 to 1. The three corners of the triangle represent the three pure components.

Since only two compositions define the composition of a stream, the stream can be located on this diagram by entering the appropriate coordinates. For example, Figure 1.10 shows the location of stream *F* that is a ternary mixture of 20 mol% *n*-butane (C4), 50 mol% *n*-pentane (C5), and 30 mol% *n*-hexane (C6).

One of the most useful and interesting aspects of ternary diagrams is the “ternary mixing rule,” which states that if two ternary streams are mixed together (one is stream *D* with composition x_{D1} and x_{D2} and the other is stream *B* with composition x_{B1} and x_{B2}), the mixture has a composition (z_1 and z_2) that lies on a **straight** line in a x_1 - x_2 ternary diagram that connects the x_D and x_B points.

Figure 1.11 illustrates the application of this mixing rule to a distillation column. Of course, a column *separates* instead of *mixes*, but the geometry is exactly the same. The two products *D* and *B* have compositions located at point (x_{D1} - x_{D2}) and (x_{B1} - x_{B2}), respectively. The feed *F* has a composition located at point (z_1 - z_2) that lies on a straight line joining *D* and *B*.

This geometric relationship is derived from the overall molar balance and the two overall component balances around the column:

$$\begin{aligned} F &= D + B \\ Fz_1 &= Dx_{D1} + Bx_{B1} \\ Fz_2 &= Dx_{D2} + Bx_{B2} \end{aligned}$$

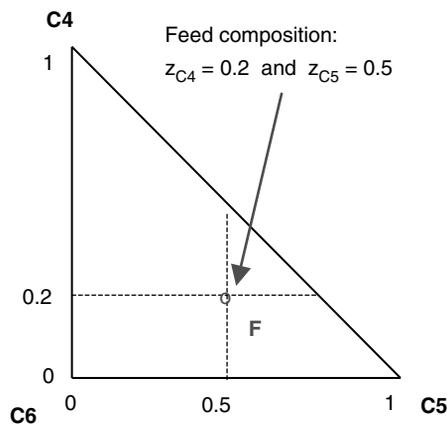


Figure 1.10 Ternary diagram.

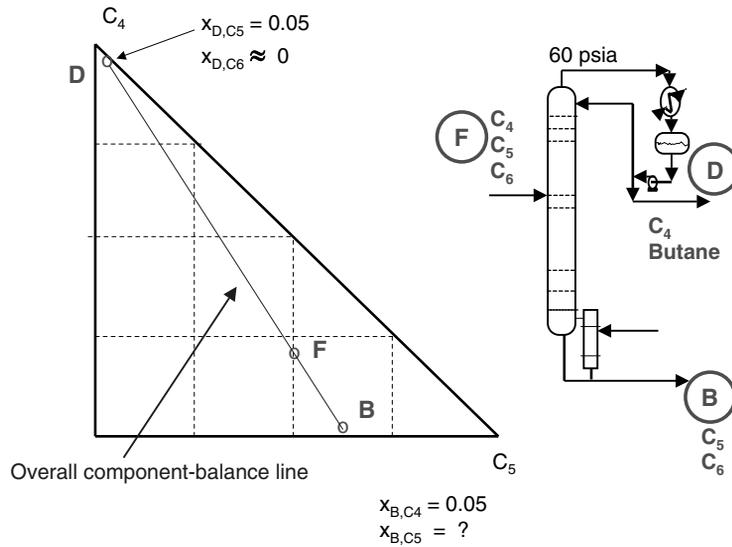


Figure 1.11 Ternary mixing rule.

Substituting the first equation in the second and third gives

$$(D + B)z_1 = Dx_{D1} + Bx_{B1}$$

$$(D + B)z_2 = Dx_{D2} + Bx_{B2}$$

Rearranging these two equations to solve for the ratio of *B* over *D* gives

$$\frac{D}{B} = \frac{z_1 - x_{D1}}{x_{B1} - z_1}$$

$$\frac{D}{B} = \frac{z_2 - x_{D2}}{x_{B2} - z_2}$$

Equating these two equations and rearranging give

$$\frac{z_1 - x_{D1}}{x_{B1} - z_1} = \frac{z_2 - x_{D2}}{x_{B2} - z_2}$$

$$\frac{x_{D1} - z_1}{z_2 - x_{D2}} = \frac{z_1 - x_{B1}}{x_{B2} - z_2}$$

Figure 1.12 shows how the ratios given above can be defined in terms of the tangents of the angles θ_1 and θ_2 . The conclusion is that both angles must be equal, so the line between *D* and *B* must pass through *F*.

As we will see in subsequent chapters, this straight-line relationship is quite useful in representing what is going on in a ternary distillation system.

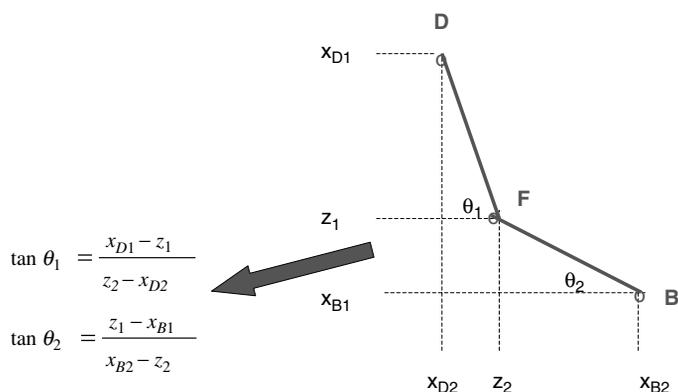


Figure 1.12 Proof of collinearity.

1.7 VLE NONIDEALITY

Liquid-phase ideality (activity coefficients $\gamma_j = 1$) occurs only when the components are quite similar. The benzene/toluene system is a common example. As shown in the sixth and seventh columns in Figure 1.5, the activity coefficients of both benzene and toluene are very close to unity.

However, if components are dissimilar, nonideal behavior occurs. Consider a mixture of methanol and water. Water is very polar. Methanol is polar on the OH end of the molecule, but the CH_3 end is nonpolar. This results in some nonideality. Figure 1.13a gives the xy curve at 1 atm. Figure 1.13b gives a table showing how the activity coefficients of the two components vary over composition space. The Unifac physical property method is used. The γ values range up to 2.3 for methanol at the $x = 0$ limit and 1.66 for water at $x = 1$. A plot of the activity coefficients can be generated by selecting the *Gamma* picture when using the *Plot Wizard*. The resulting plot is given in Figure 1.13c.

Now consider a mixture of ethanol and water. The $\text{CH}_3\text{-CH}_2$ end of the ethanol molecule is more nonpolar than the CH_3 end of methanol. We would expect the nonideality to be more pronounced, which is exactly what the Txy diagram, the activity coefficient results, and the xy diagram given in Figure 1.14 show.

Note that the activity coefficient of ethanol at the $x = 0$ end (pure water) is very large ($\gamma_{\text{EtOH}} = 6.75$) and also that the xy curve shown in Figure 1.14c crosses the 45° line ($x = y$) at ~ 90 mol% ethanol. This indicates the presence of an azeotrope. Note also that the temperature at the azeotrope (351.0 K) is lower than the boiling point of ethanol (351.5 K).

An “azeotrope” is defined as a composition at which the liquid and vapor compositions are equal. Obviously, when this occurs, there can be no change in the liquid and vapor compositions from tray to tray in a distillation column. Therefore an azeotrope represents a “distillation boundary.”

Azeotropes occur in binary, ternary, and multicomponent systems. They can be “homogeneous” (single liquid phase) or “heterogeneous” (two liquid phases). They can be “minimum boiling” or “maximum boiling.” The ethanol/water azeotrope is a minimum-boiling homogeneous azeotrope.

The software Aspen Split provides a convenient method for calculating azeotropes. Go to *Tools* on the top toolbar, then select *Aspen Split* and *Azeotropic Search*. The window shown at the top of Figure 1.15 opens, on which the components and pressure level are specified. Clicking on *Azeotropes* opens the window shown at the bottom of Figure 1.15, which gives the calculated results: a homogeneous azeotrope at 78°C (351 K) with composition 89.3 mol% ethanol.

Up to this point we have been using *Split* as an analysis tool. Aspen Technology plans to phase out *Split* in new releases of their Engineering Suite and will offer another tool called “DISTIL,” which has more capability. To illustrate some of the features of DISTIL, let us use it to study a system in which there is more dissimilarity of the molecules

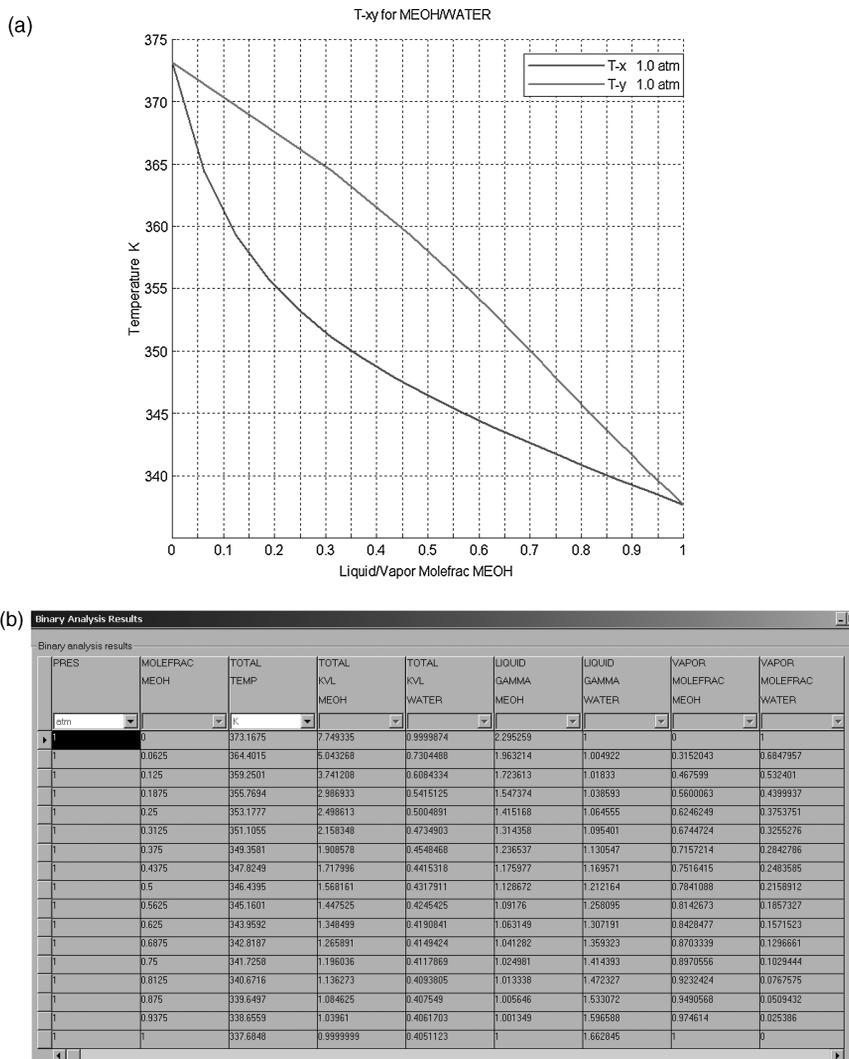


Figure 1.13 (a) Txy diagram for methanol/water; (b) activity coefficients for methanol/water; (c) activity coefficient plot for methanol/water.

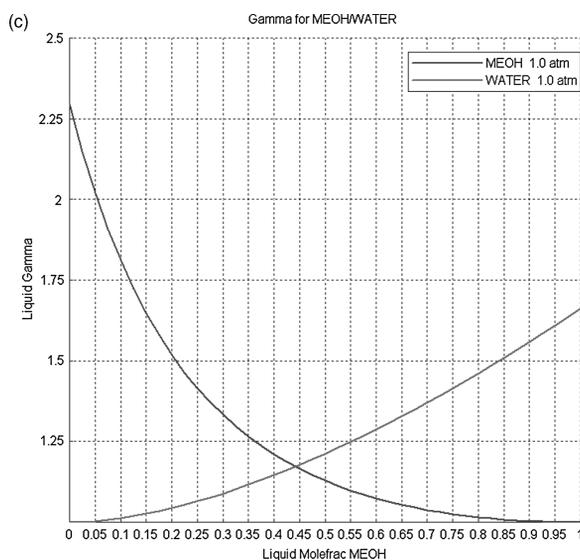


Figure 1.13 Continued.

by looking at the *n*-butanol/water system. The normal boiling point of *n*-butanol is 398 K, while that of water is 373 K, so water is the low boiler in this system.

The DISTIL program is opened in the usual way. Clicking the *Managers* button on the top toolbar of the DISTIL window and clicking *Fluid Package Manager* opens the window shown at the top of Figure 1.16. Click the *Add* button. The window shown at the bottom of Figure 1.16 opens. On the *Property Package* page tab, the UNIFAC VLE package is selected with *Ideal Gas*. Then click the *Select* button on the right side of the window.

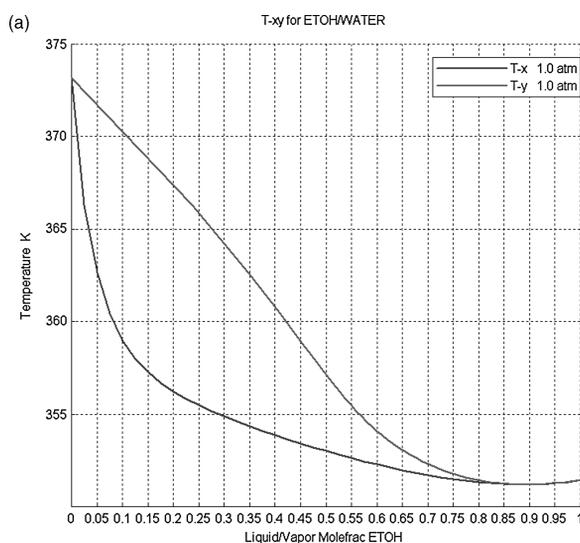


Figure 1.14 T_{xy} diagram for ethanol/water (a), activity coefficient plot (b), and xy plot (c) for ethanol/water.

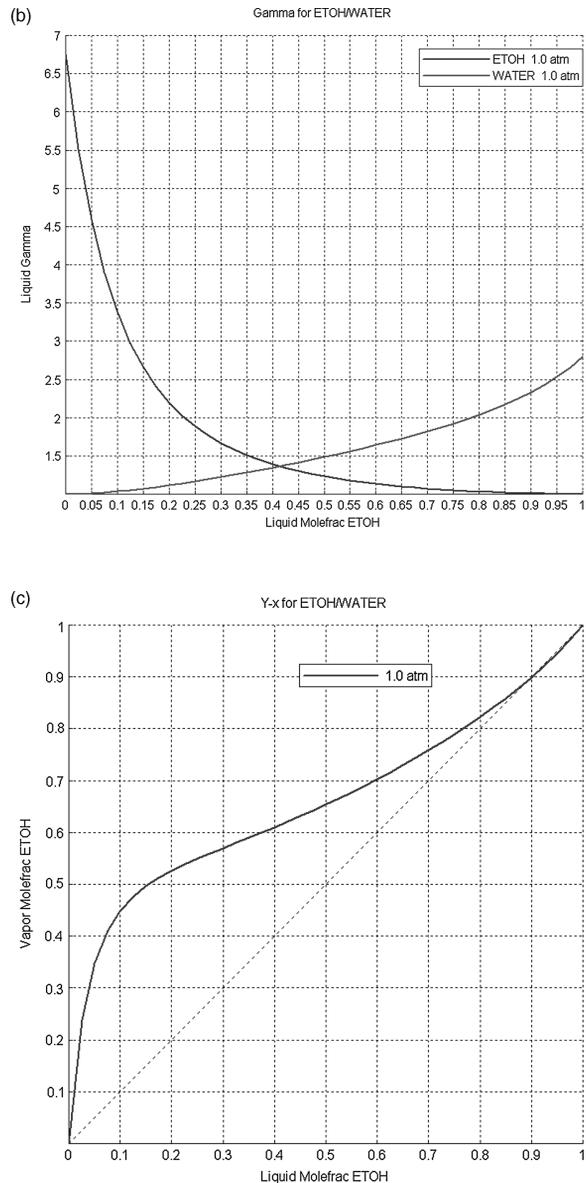


Figure 1.14 Continued.

Next click the *Components* page tab. Enter the name of a component in the *Matches* window and click *Select* to add each component to list on the left, as shown at the top of Figure 1.17.

Now click the *Manager* button again on the top toolbar and select *Separation Manager—Separation and Azeotrope Analysis*, which opens the window shown at the bottom Figure 1.17. With the *Fluid Package* highlighted under the *Setup* column on the left, the physical property package to be used is selected from the dropdown menu, and the components of interest are selected by clicking under the *Selected* column to

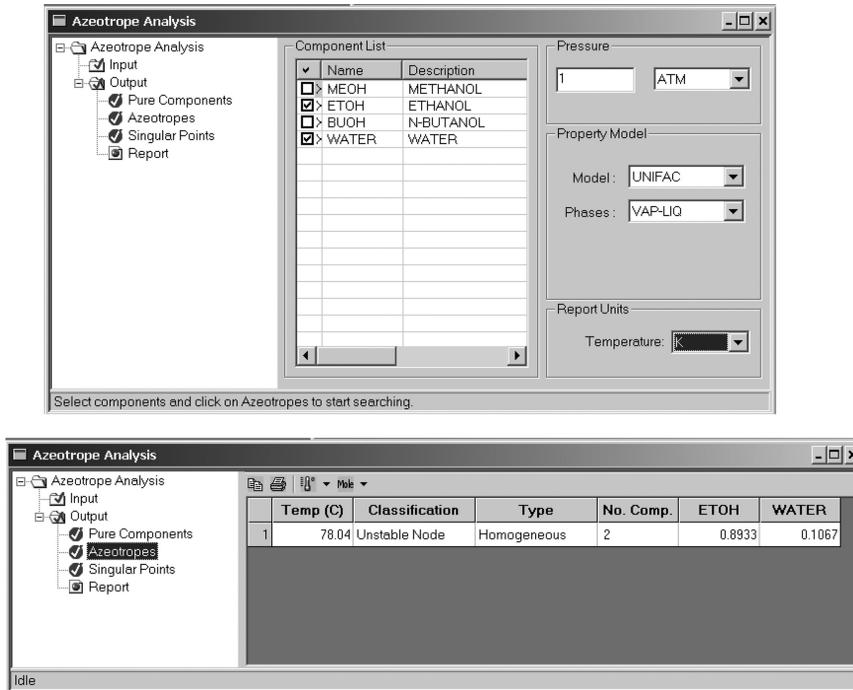


Figure 1.15 Aspen Split ethanol/water.

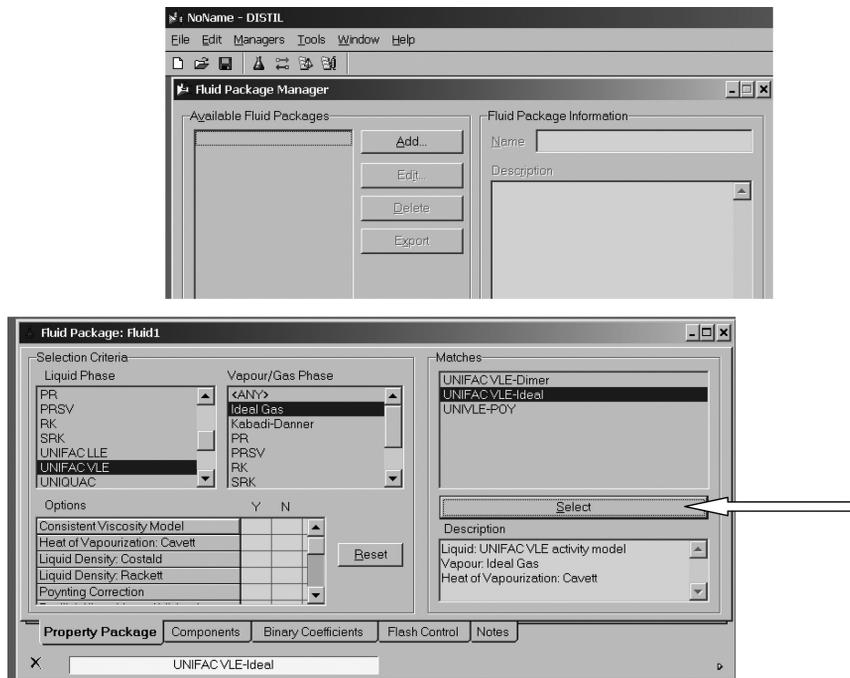


Figure 1.16 Setting up fluid package in DISTIL.

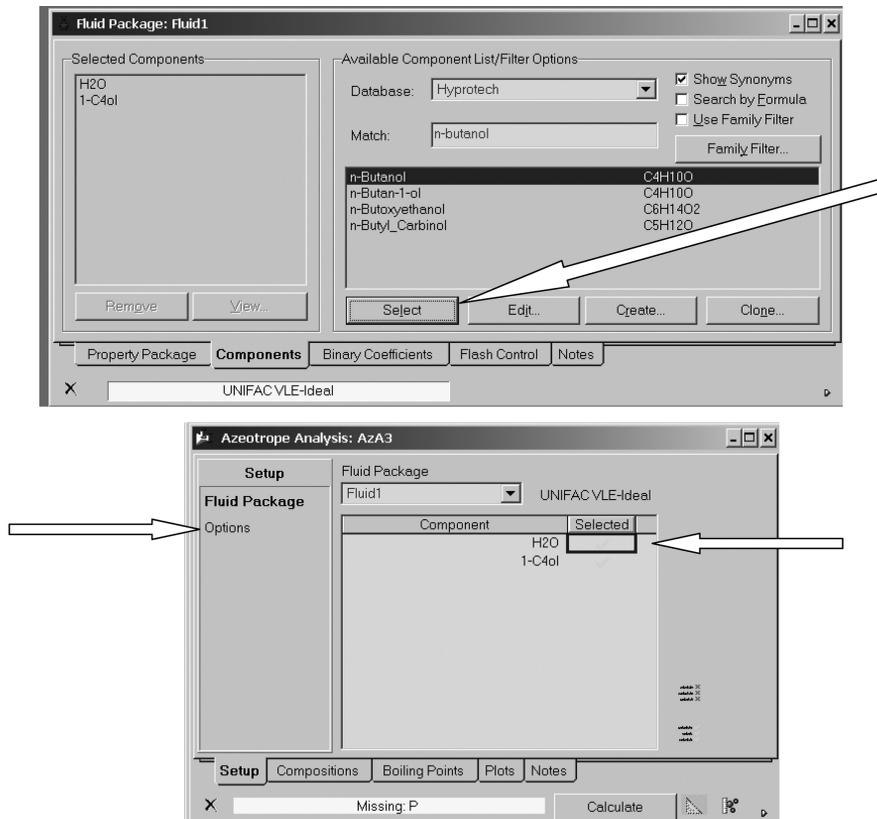


Figure 1.17 Selecting components in DISTIL.

place a green checkmark, not a red “x.” Note that there is a message in the yellow box at the bottom of the window stating that the pressure needs to be specified. Clicking *Options* under the *Setup* column on the left opens the window shown at the top of Figure 1.18, where the pressure or a range of pressures is specified. Then click the *Calculate* button at the bottom of the window. Selecting the *Compositions* page tab or the *Boiling Points* page tab gives the results shown in Figure 1.19. Note that the azeotropic temperature (93°C) is lower than the boiling points of pure water (100°C) or butanol (118°C).

Various types of diagrams can be generated by going to the top toolbar and selecting *Managers*, *Thermodynamic Workbench Manager*, and *Phase Equilibrium Properties*. The window given at the top of Figure 1.20a opens, on which the fluids package and component are selected. Clicking the *Plots* page tab opens the window shown at the bottom of Figure 1.20a, on which pressure is set and the type of plot is specified. A *Txy* diagram is selected. Figure 1.20b gives activity coefficient and *xy* plots.

These results show a huge activity coefficient for butanol ($\gamma_{\text{BuOH}} = 40$) at the $x = 1$ point. The horizontal lines in the *Txy* diagram and the *xy* diagram indicate the presence of an heterogeneous azeotrope. The molecules are so dissimilar that two liquid phases are formed. At the azeotrope, the vapor composition is ~76 mol% water and the compositions of the two liquid phases are ~50 and ~97 mol% water.

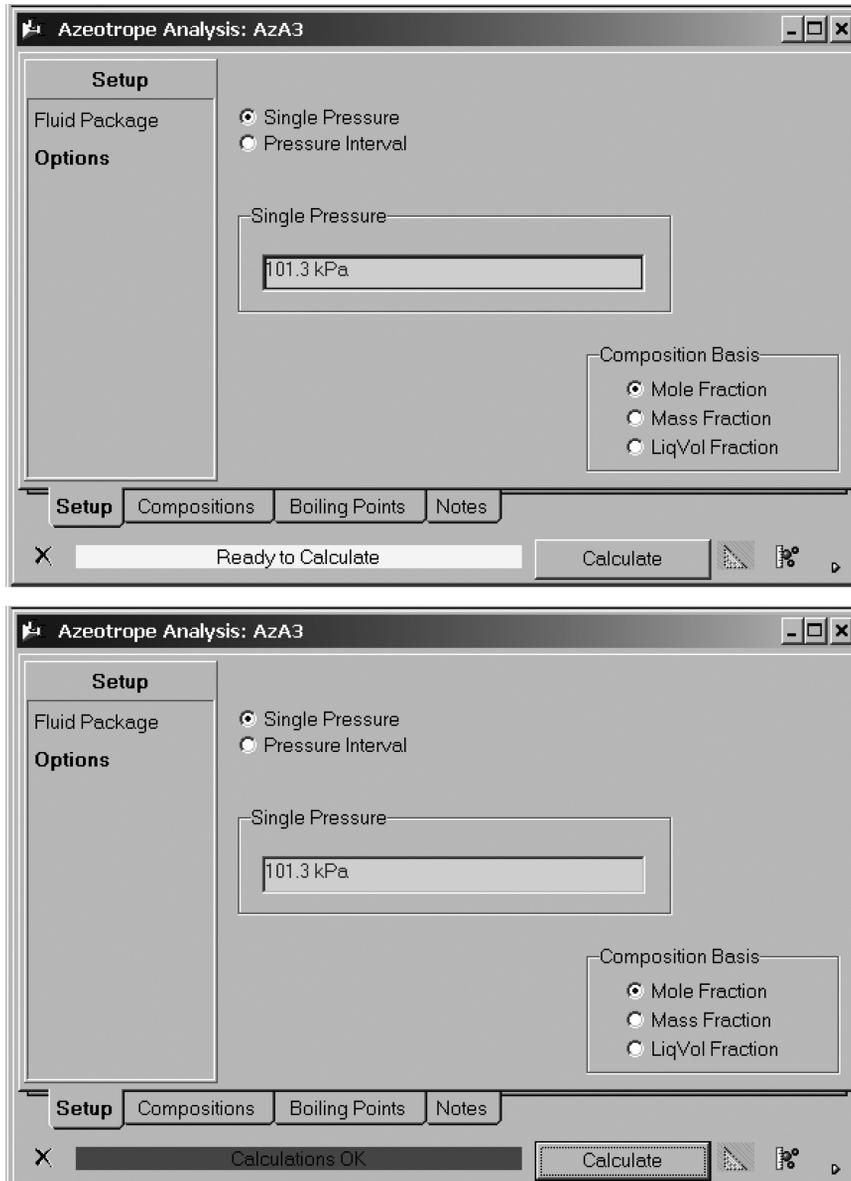


Figure 1.18 Specifying pressure.

Up to this point we have considered only binary systems. In the following section ternary nonideal systems are explored using the capabilities of Aspen Split.

1.8 RESIDUE CURVES FOR TERNARY SYSTEMS

Residue curve analysis is quite useful in studying ternary systems. A mixture with an initial composition $x_{1(0)}$ and $x_{2(0)}$ is placed in a container at some fixed pressure. A

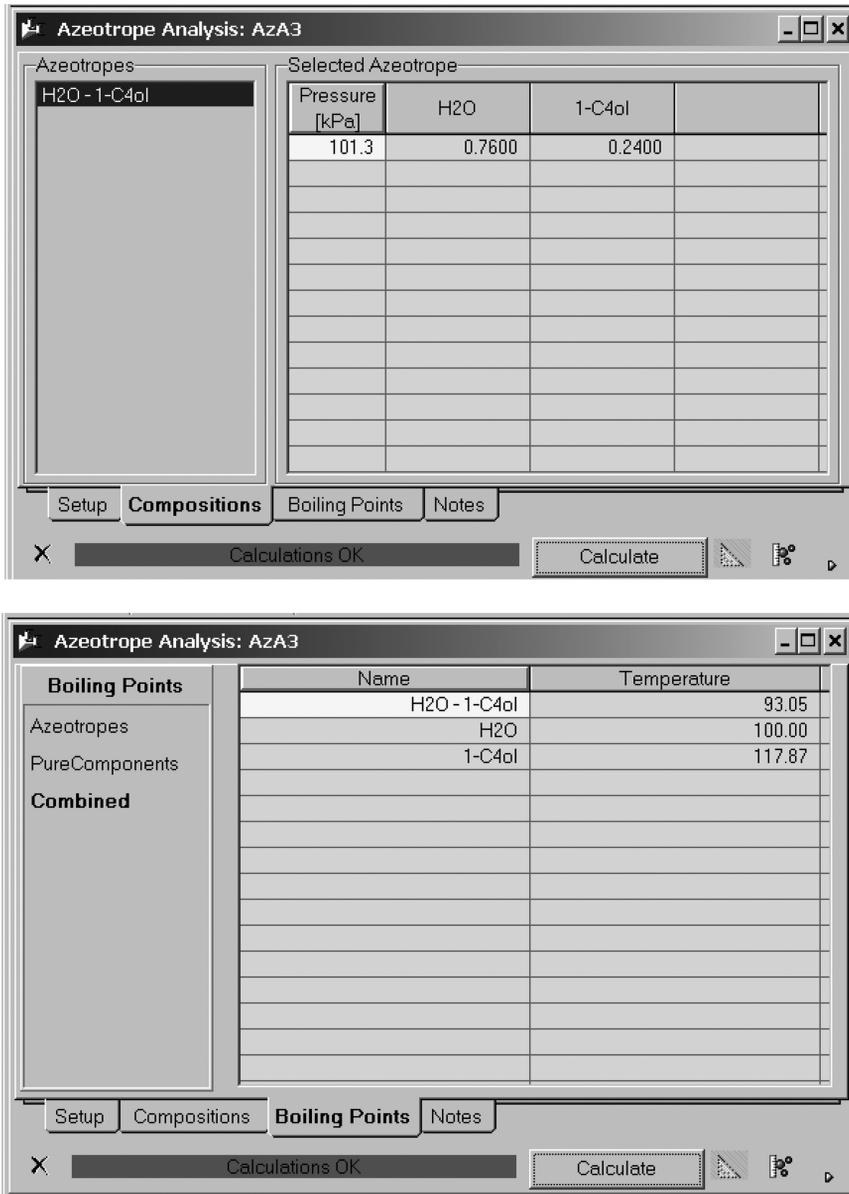


Figure 1.19 Azeotrope composition and temperatures.

vapor stream is continuously removed, and the composition of the remaining liquid in the vessel is plotted on the ternary diagram.

Figure 1.21 gives an example of how the compositions of the liquid x_j and the vapor y_j change with time during this operation. The specific numerical example is a ternary mixture of components A, B, and C, which have constant relative volatilities of $\alpha_A = 4$,

$\alpha_B = 2$, and $\alpha_C = 1$. The initial composition of the liquid is $x_A = 0.5$ and $x_B = 0.25$. The initial amount of liquid is 100 mol, and vapor is withdrawn at a rate of 1 mol per unit of time. Note that component A is quickly depleted from the liquid because it is the lightest component. The liquid concentration of component B actually increases for a while and then drops. Figure 1.22 plots the x_A and x_B trajectories for different initial conditions. These are the “residue curves” for this system.

Residue curves can be easily generated by using Aspen Split. Click on *Tools* in the upper toolbar in the *Aspen Plus* window and select *Aspen Split* and *Ternary Maps*. This opens the window shown in Figure 1.23, on which the three components and pressure

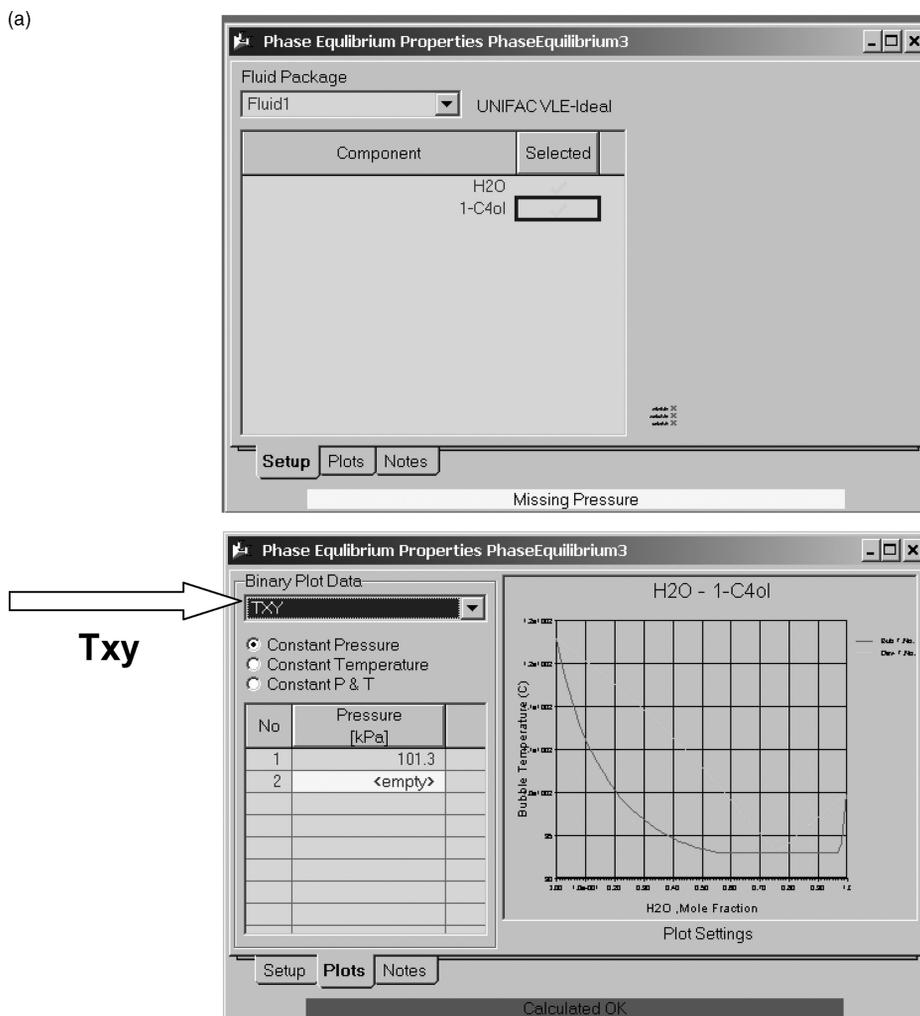


Figure 1.20 Generating VLE diagrams.

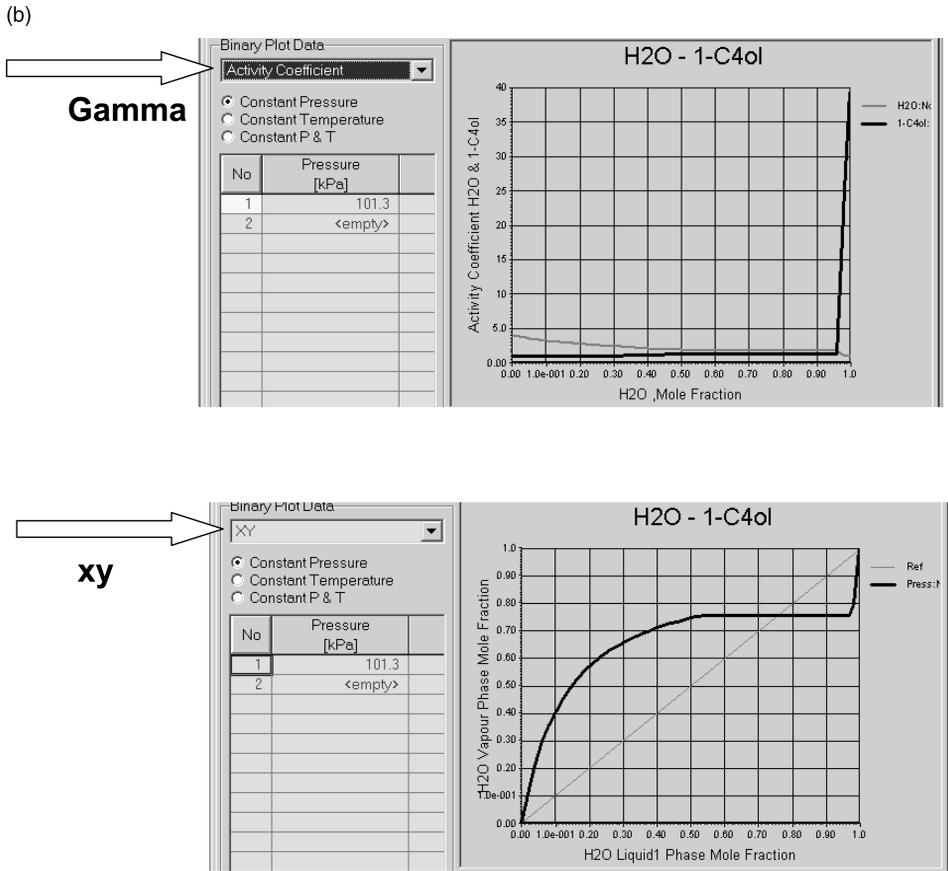


Figure 1.20 Continued.

are selected. The numerical example is the ternary mixture of *n*-butane, *n*-pentane, and *n*-hexane. Clicking on *Ternary Plot* opens the window given in Figure 1.24. To generate a residue curve, right-click the diagram and select *Add* and *Curve*. A crosshair appears that can be moved to any location on the diagram. Clicking inserts a residue curve that passes through the selected point, as shown in Figure 1.25a. Repeating this procedure produces multiple residue curves as shown in Figure 1.25b.

Note that all the residue curves start at the lightest component (C4) and move toward the heaviest component (C6). In this sense they are similar to the compositions in a distillation column. The light components go out the top, and the heavy components, go out the bottom. We will show below that this similarity proves to be useful for the analysis of distillation systems.

The generation of residue curves is described mathematically by a dynamic molar balance of the liquid in the vessel M_{liq} and two dynamic component balances for

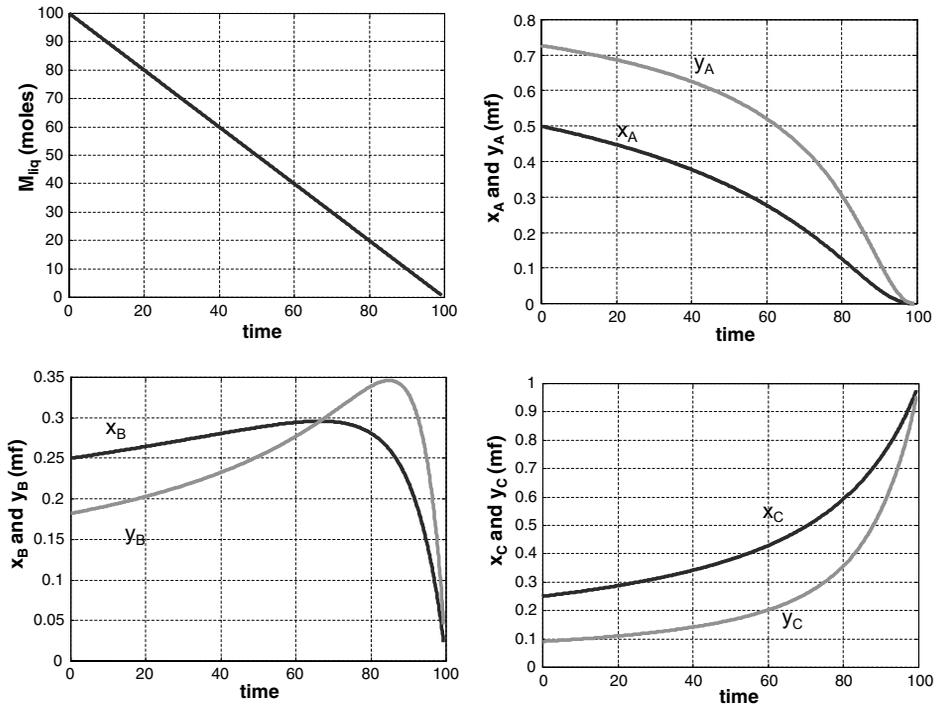


Figure 1.21 Generation of residue curves.

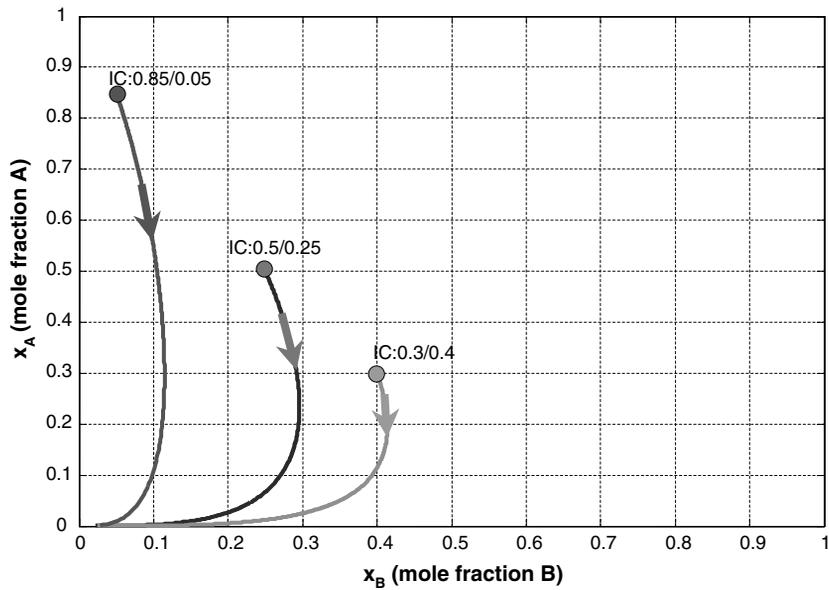


Figure 1.22 Residue curves starting from different initial conditions.

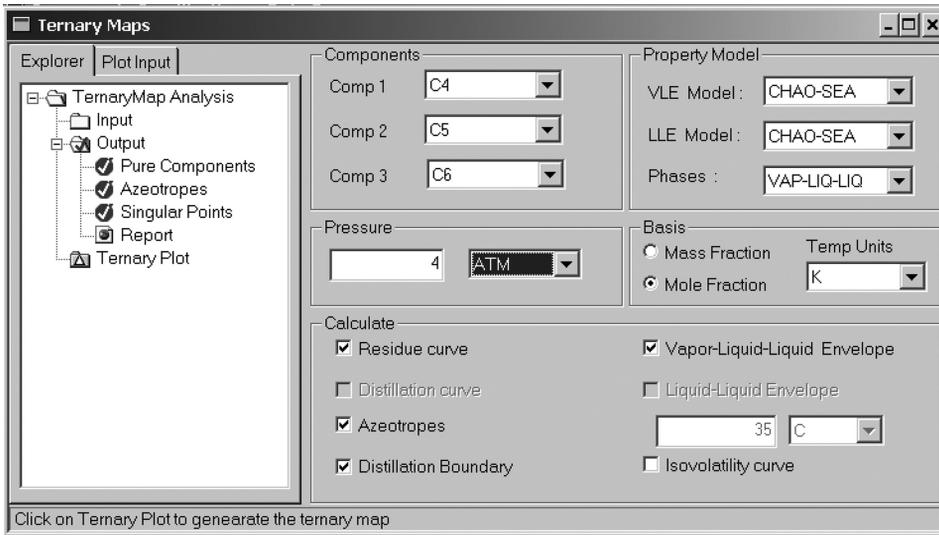


Figure 1.23 Setting up ternary maps in Aspen Split.

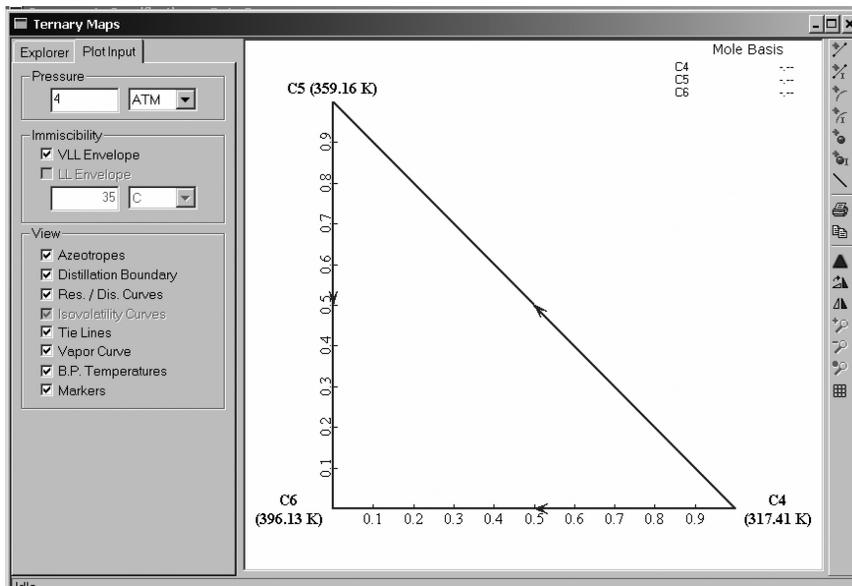


Figure 1.24 Ternary diagram for C4, C5, and C6.

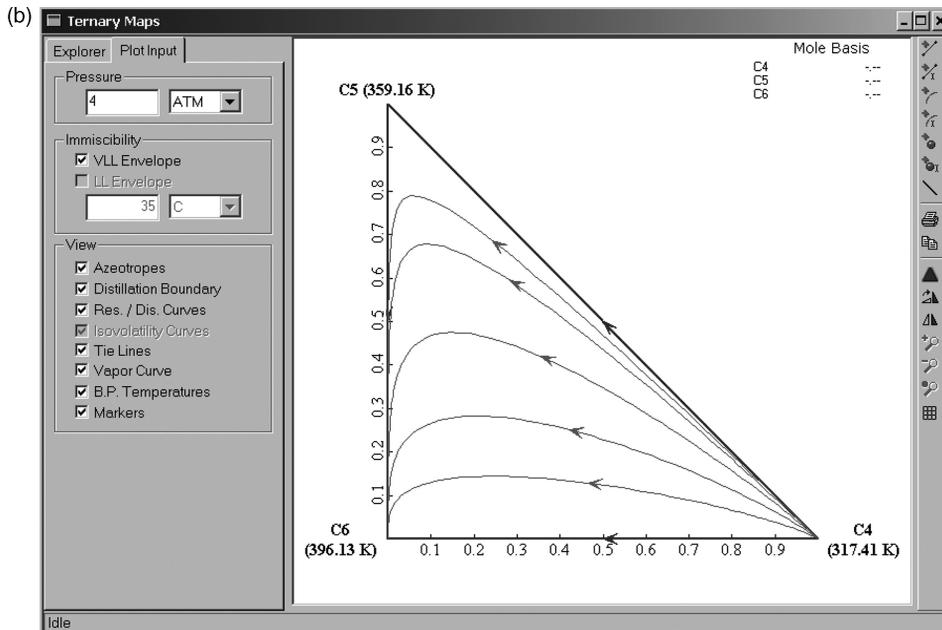
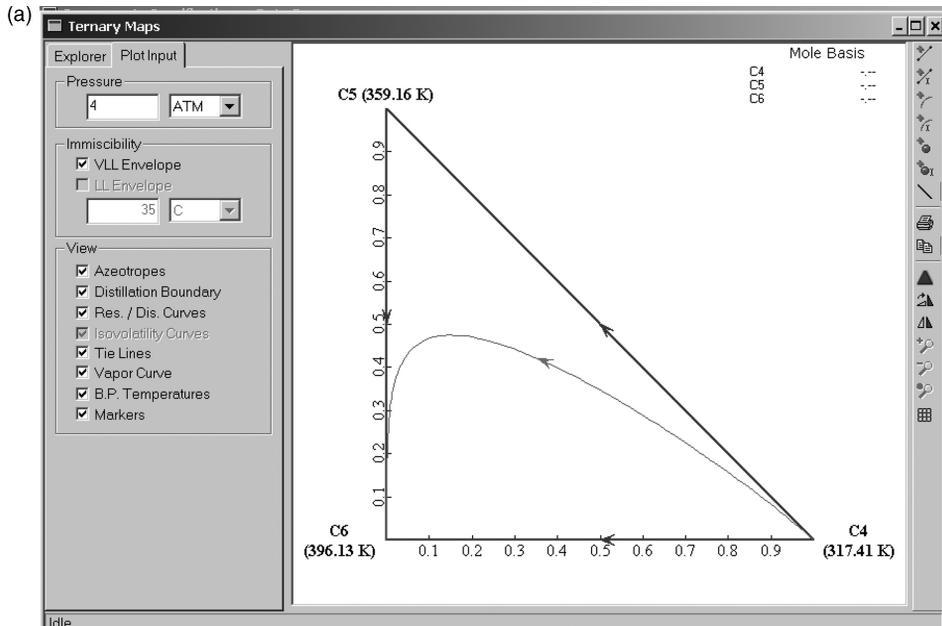


Figure 1.25 (a) Adding a residue curve; (b) several residue curves.

components A and B. The rate of vapor withdrawal is V (moles per unit time):

$$\frac{dM_{\text{liq}}}{dt} = -V$$

$$\frac{d(M_{\text{liq}}x_j)}{dt} = -Vy_j$$

Of course, the values of x_j and y_j are related by the VLE of the system. Expanding the second equation and substituting the first equation give

$$M_{\text{liq}} \frac{dx_j}{dt} + x_j \frac{dM_{\text{liq}}}{dt} = -Vy_j$$

$$M_{\text{liq}} \frac{dx_j}{dt} + x_j(-V) = -Vy_j$$

$$\left(\frac{M_{\text{liq}}}{V}\right) \frac{dx_j}{dt} = x_j - y_j$$

$$\frac{dx_j}{d\theta} = x_j - y_j$$

The parameter θ is a dimensionless time variable. The last equation models how compositions change during the generation of a residue curve. As we describe below, a similar equation expresses the tray-to-tray liquid compositions in a distillation column under total reflux conditions. This relationship permits us to use residue curves to assess which separations are feasible or infeasible in a given system.

Consider the upper section of a distillation column as shown in Figure 1.26. The column is cut at tray n , at which the passing vapor and liquid streams have compositions

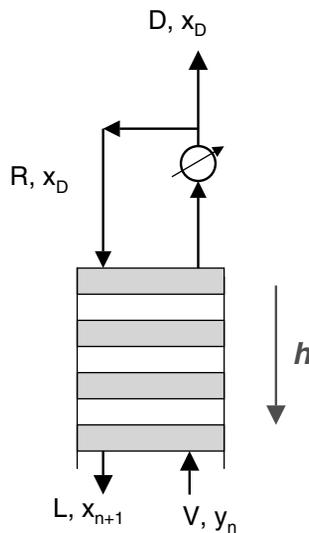


Figure 1.26 Distillation column.

y_{nj} and $x_{n+1,j}$ and flowrates are V_n and L_{n+1} . The distillate flowrate and composition are D and x_{Dj} . The steady-state component balance is

$$V_n y_{nj} = L_{n+1} x_{n+1,j} + D x_{Dj}$$

Under total reflux conditions, D is equal to zero and L_{n+1} is equal to V_n . Therefore y_{nj} is equal to $x_{n+1,j}$.

Let us define a continuous variable h as the distance from the top of the column down to any tray. The discrete changes in liquid composition from tray to tray can be approximated by the differential equation

$$\frac{dx_j}{dh} \approx x_{nj} - x_{n+1,j}$$

At total reflux this equation becomes

$$\frac{dx_j}{dh} = x_{nj} - y_{nj}$$

Note that this is the same equation as developed for residue curves.

The significance of this similarity is that the residue curves approximate the column profiles. Therefore a feasible separation in a column must satisfy two conditions:

1. The distillate compositions x_{Dj} and the bottoms compositions x_{Bj} must lie near a residue curve.
2. They must lie on a straight line through the feed composition point z_j .

We will use these principles in Chapters 2 and 5 for analyzing both simple and complex distillation systems.

1.9 CONCLUSION

The basics of vapor-liquid phase equilibrium have been reviewed in this chapter. A good understanding of VLE is indispensable in the design and control of distillation systems. These basics will be used throughout this book.