

CHAPTER 1

FUNDAMENTALS OF VAPOR–LIQUID 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 equilibrium (VLE) and in some cases vapor–liquid–liquid equilibrium (VLLE). Distillation can only effect a separation among chemical components 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 there are both liquid and vapor phases 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 is plotted against the reciprocal of the absolute temperature. As temperature increases, we move to the left in the figure, which

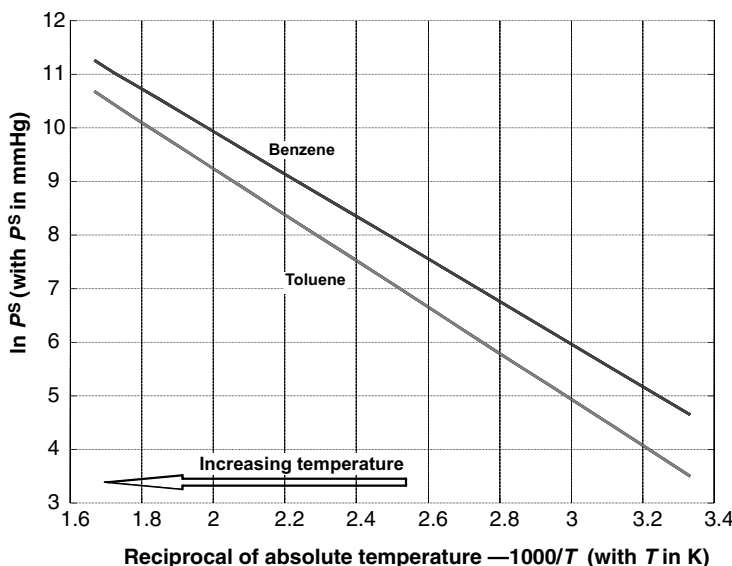


Figure 1.1 Vapor pressures of pure benzene and toluene.

means a higher vapor pressure. In this particular figure, the vapor pressure P^S of each component is given in units of mmHg. The temperature is given in kelvin.

Looking at a vertical constant-temperature line shows that benzene has a higher vapor pressure than 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 toluene. Therefore, benzene is the “lower-boiling” component. Notice 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 vapor phase will contain a higher concentration of benzene than will 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, atm, etc.) and on the units used for temperature (K or °R).

1.2 BINARY VLE PHASE DIAGRAMS

There are two types of VLE diagrams that are widely used to represent data for two-component (binary) systems. The first is a “temperature versus x and y ” diagram (T_{xy}). The x term represents the liquid composition, usually 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. Because the pressure in a distillation column is relatively constant in most column (the exception is vacuum distillation in which the pressure at the top and bottom are significantly different in terms of absolute pressure level), a T_{xy} diagram and an xy diagram are convenient for the analysis of binary distillation systems.

Figure 1.2 gives the T_{xy} diagram for the benzene/toluene system at a pressure of 1 atm. The abscissa is the mole fraction of benzene. The ordinate is temperature. The lower curve is the “saturated liquid” line that gives the mole fraction of benzene in the liquid phase x . The upper curve is the “saturated vapor” line that 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 mol fraction benzene, and the value of y is 0.586 mol fraction benzene. As expected, the vapor is richer in the lighter component.

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

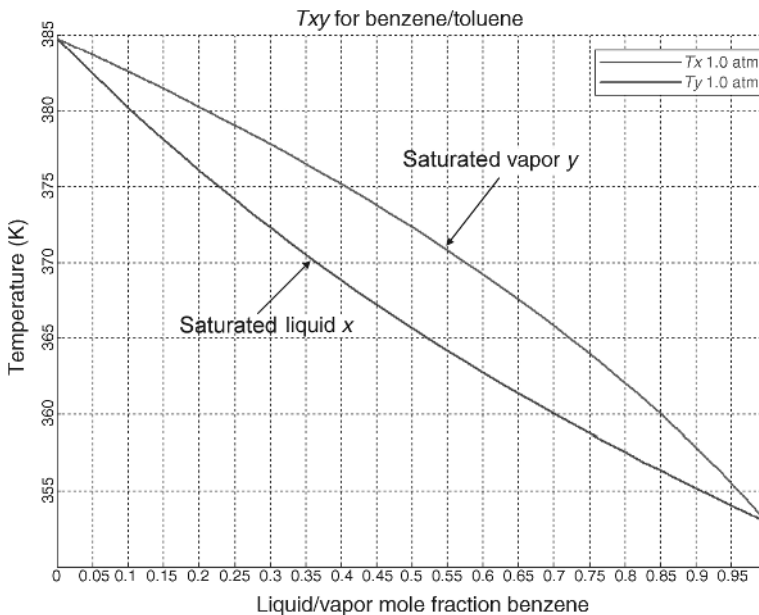


Figure 1.2 T_{xy} diagram for benzene and toluene at 1 atm.

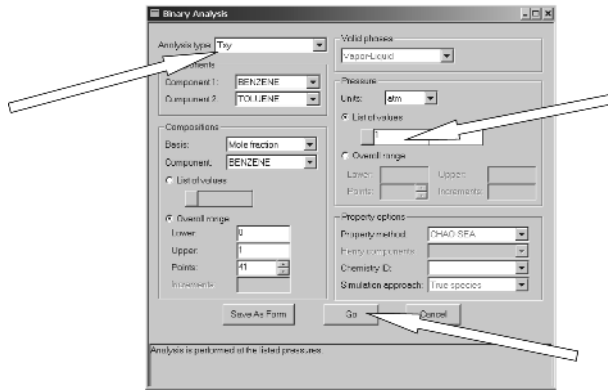


Figure 1.3 Specifying Txy diagram parameters.

The diagram is easily generated in Aspen Plus by going to *Tools* on the upper tool bar and selecting *Analysis*, *Property*, and *Binary*. The window shown in Figure 1.3 opens on which the type of diagram and the pressure are specified. Then 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 temperature.

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

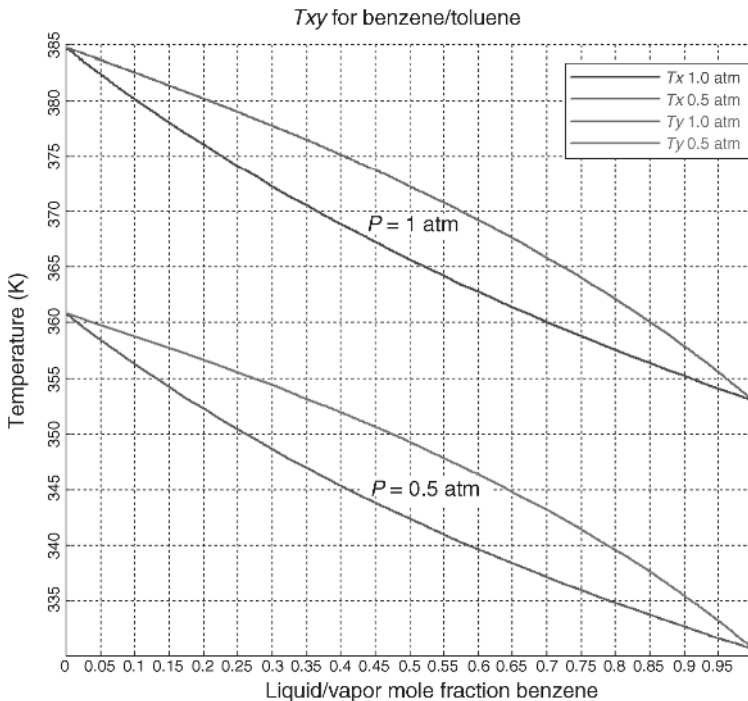


Figure 1.4 Txy diagrams at two pressures.

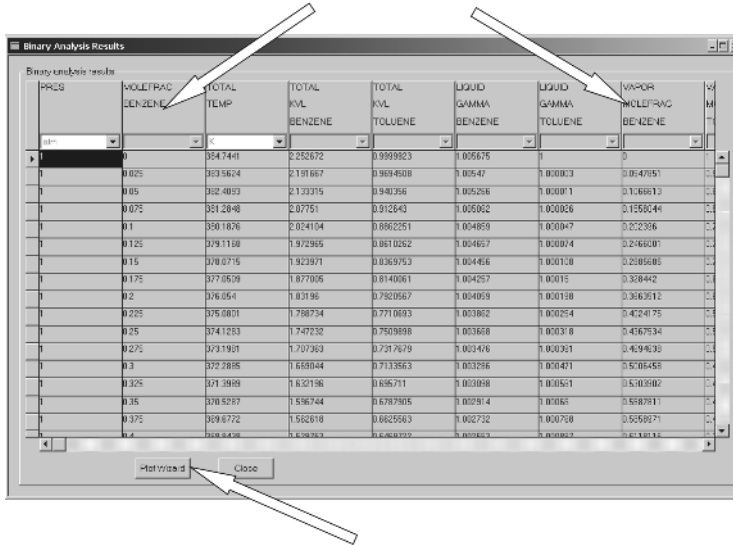


Figure 1.5 Using Plot Wizard to generate xy diagram.

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 *xy* picture is selected. Clicking the *Next* and *Finish* button generates the *xy* diagram shown in Figure 1.7. Figure 1.8 gives an *xy* diagram for the system propylene/propane. These components have boiling points that are quite close, which leads to a very difficult separation.

These diagrams provide valuable insight about 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.

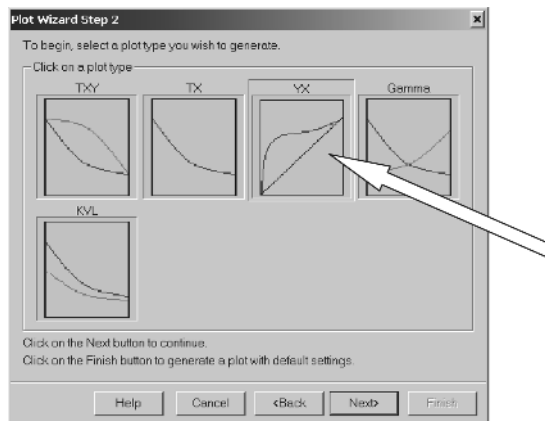


Figure 1.6 Using Plot Wizard to generate xy diagram.

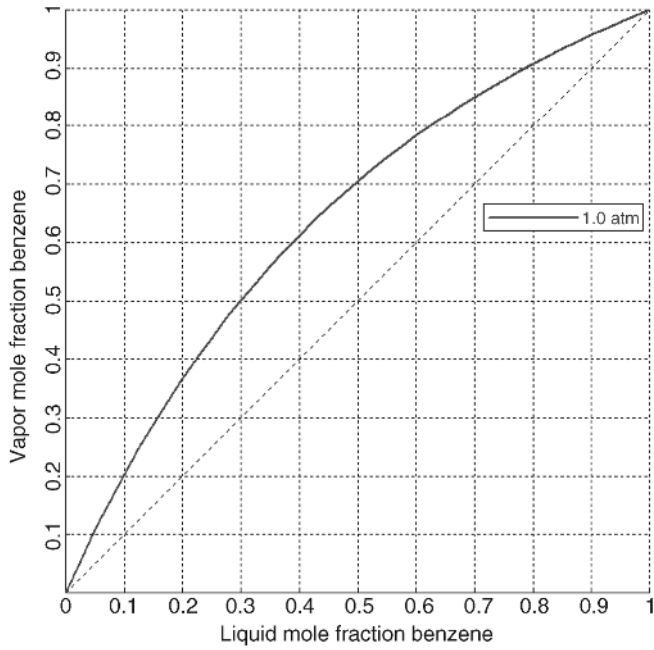


Figure 1.7 xy diagram for benzene/toluene.

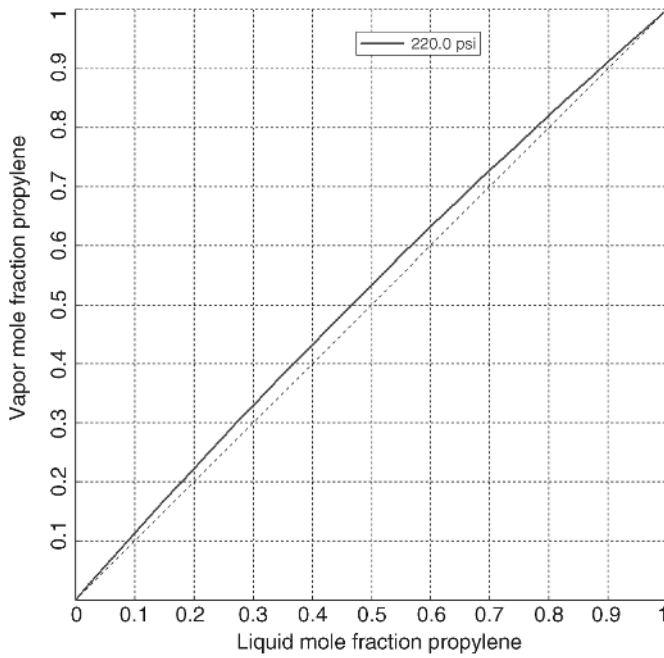


Figure 1.8 xy diagram for propylene/propane.

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, it can be used to determine what physical property method fits the column data. There could be a problem in using column data because the tray efficiency is also not known, 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 the use of “relative volatility.” The definition of relative volatility is the ratio of the y/x values (vapor mole fraction over liquid mole fraction) of two components. For example, the relative volatility of component L with respect to component H is defined in the equation below.

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

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 component and the heavy component 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).

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

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

In the multicomponent case, a similar relationship can be derived. Suppose 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 .

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

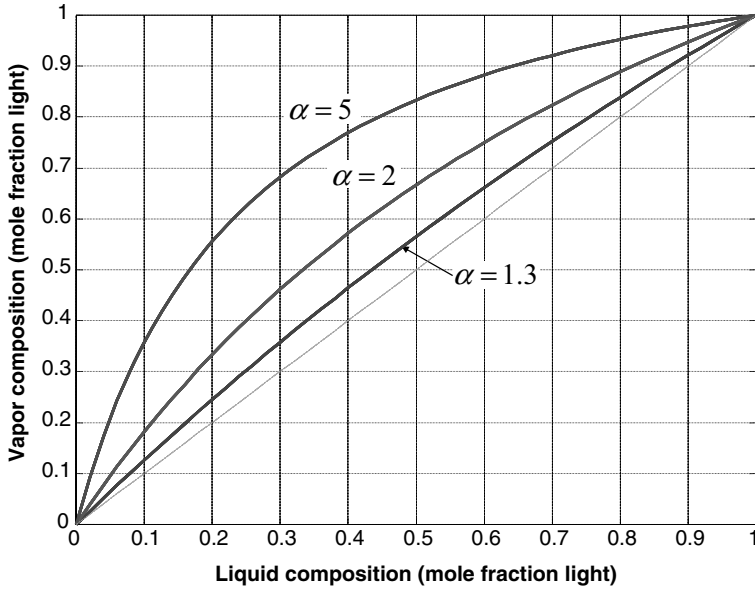


Figure 1.9 xy curves for relative volatilities of 1.3, 2, and 5.

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

$$y_j = \alpha_j x_j (y_H/x_H)$$

$$\sum_{j=1}^{NC} y_j = 1 = \sum_{j=1}^{NC} \alpha_j x_j (y_H/x_H)$$

$$1 = (y_H/x_H) \sum_{j=1}^{NC} \alpha_j x_j$$

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

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

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

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 Section 1.5.

1.5 BUBBLE POINT 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 of the x_j). 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” (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

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

The total pressure P and all the x_j 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^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 abscissa is the mole fraction of component 1. The ordinate is the mole fraction of component 2. 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, it 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.” This 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

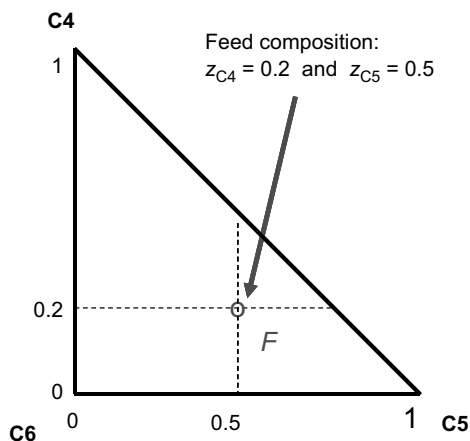


Figure 1.10 Ternary diagram.

mixture has a composition (z_1 and z_2) that lies on a *straight* line in 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 point ($x_{B1}-x_{B2}$), respectively. The feed F has a composition located at point (z_1-z_2) that lies on a straight line joining D and B .

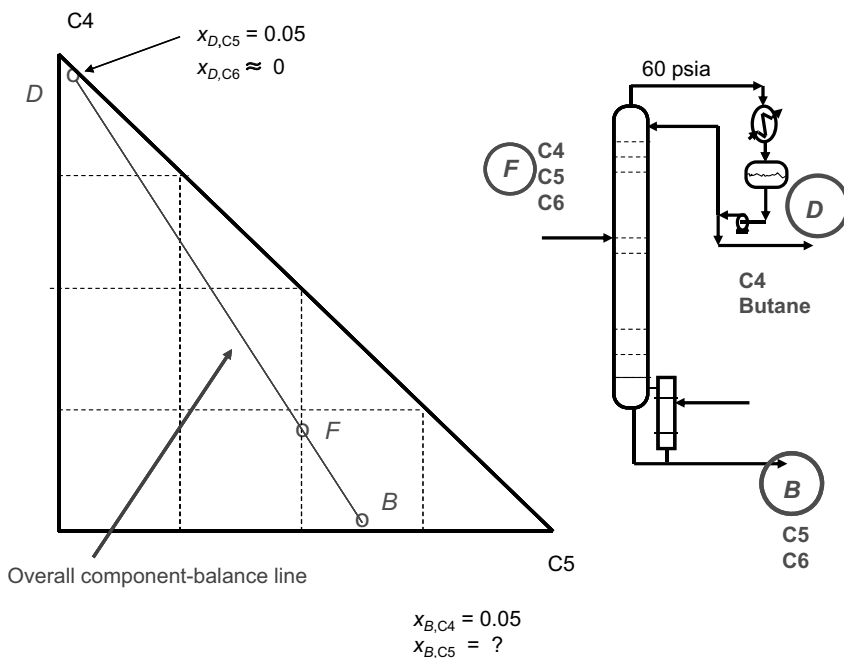


Figure 1.11 Ternary mixing rule.

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

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

Substituting the first equation into the second and third gives

$$\begin{aligned}(D + B)z_1 &= Dx_{D1} + Bx_{B1} \\(D + B)z_2 &= Dx_{D2} + Bx_{B2}\end{aligned}$$

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

$$\begin{aligned}\frac{D}{B} &= \frac{(z_1 - x_{D1})}{(x_{B1} - z_1)} \\ \frac{D}{B} &= \frac{(z_2 - x_{D2})}{(x_{B2} - z_2)}\end{aligned}$$

Equating these two equations and rearranging gives

$$\begin{aligned}\frac{z_1 - x_{D1}}{x_{B1} - z_1} &= \frac{z_2 - x_{D2}}{x_{B2} - z_2} \\ \frac{x_{D1} - z_1}{z_2 - x_{D2}} &= \frac{z_1 - x_{B1}}{x_{B2} - z_2}\end{aligned}$$

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 the two 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. This straight line is called the component-balance line.

1.7 VLE NONIDEALITY

Liquid-phase ideality (activity coefficients $\gamma_j = 1$) only occurs when the components are quite similar. The benzene/toluene system is a common example. As shown in Figure 1.5 in the sixth and seventh columns, 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 “CH₃” 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.

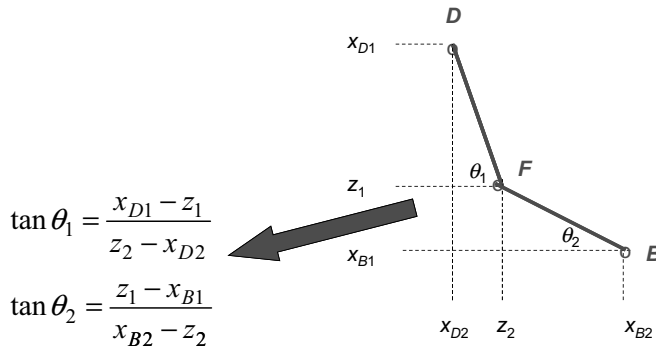


Figure 1.12 Proof of colinearity.

Now consider a mixture of ethanol and water. The “CH₃-CH₂” end of the ethanol molecule is more nonpolar than the “CH₃” 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.

Notice that the activity coefficient of ethanol at the *x* = 0 end (pure water) is very large ($\gamma_{\text{EtOH}} = 6.75$). Notice also that the *xy* curve shown in Figure 1.14c crosses the 45° line (*x* = *y*) at about 90 mol% ethanol. This indicates the presence of an “azeotrope.” Note also

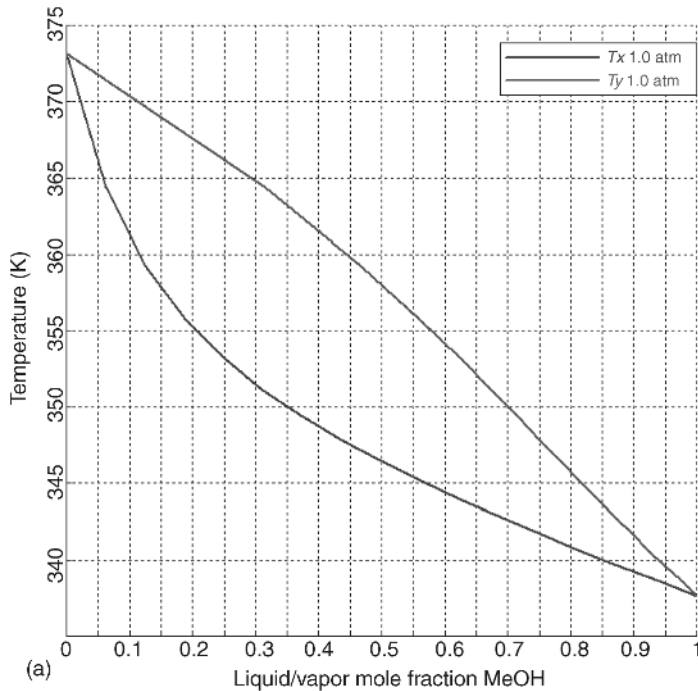


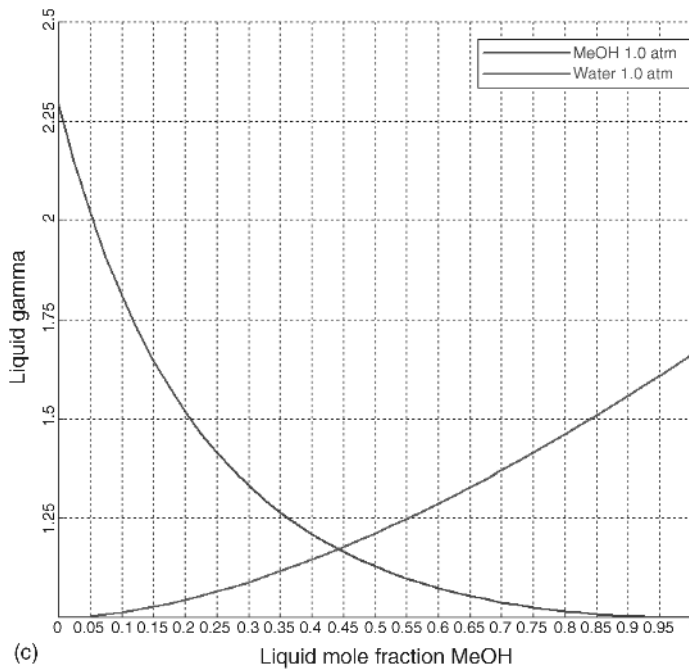
Figure 1.13 (a) *Txy* diagram for methanol/water. (b) Activity coefficients for methanol/water. (c) Activity coefficient plot for methanol/water.

Binary Analysis Results

Binary analysis results

TRAY	MOLEFRAC MEOH	TOTAL TEMP	TOTAL K _L MEOH	TOTAL K _V WALFH	LIQUID GAMMA MEOH	LIQUID GAMMA WALFH	VAPOR MOLEFRAC MEOH	VAPOR MOLEFRAC WALFH
0	0	373.1675	7.79033	0.9988274	2.291150	0	0	0
1	0.0025	364.4015	5.148533	1.2084418	0.863774	0.004822	0.332043	0.8842317
2	0.0175	360.7910	3.748731	1.6084174	0.773173	0.018351	0.487560	0.829411
3	0.1075	355.7694	2.888932	2.561115	0.67274	0.038593	0.660061	0.6993127
4	0.25	353.7777	2.490671	3.0001121	0.613100	0.064555	0.8246218	0.5953211
5	0.3175	351.7065	2.388044	3.254115	0.584388	0.088401	0.9244024	0.5256228
6	0.375	349.5691	2.366671	3.464491	0.561537	0.108427	0.9762974	0.4660191
7	0.4375	347.4640	2.377993	3.641316	0.543337	0.124971	0.9716418	0.4203218
8	0.5	346.4398	2.40111	3.801711	0.531352	0.137184	0.9440388	0.3783111
9	0.5625	345.5001	2.43925	3.947115	0.52471	0.145096	0.9145277	0.3392217
10	0.625	345.6982	2.49188	4.083211	0.52308	0.149191	0.8829377	0.3037217
11	0.6875	346.0307	2.55247	4.204214	0.526732	0.149321	0.8501111	0.2704115
12	0.75	346.5258	2.62031	4.311716	0.53431	0.144393	0.8170561	0.2393444
13	0.8125	347.1776	2.69471	4.403115	0.545320	0.132327	0.8232424	0.1997216
14	0.875	347.9497	2.774621	4.479116	0.55916	0.112072	0.8490561	0.1609112
15	0.9375	348.8009	2.85961	4.542115	0.574700	0.084674	0.874674	0.1253111
16	1	349.8881	2.930011	4.591115	0	0.062946	0	0

(b)



(c)

Figure 1.13 (Continued)

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.

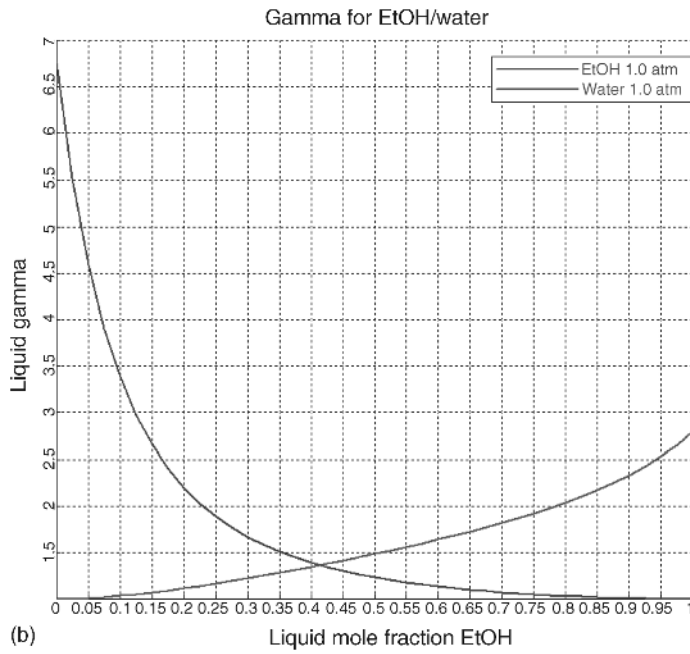
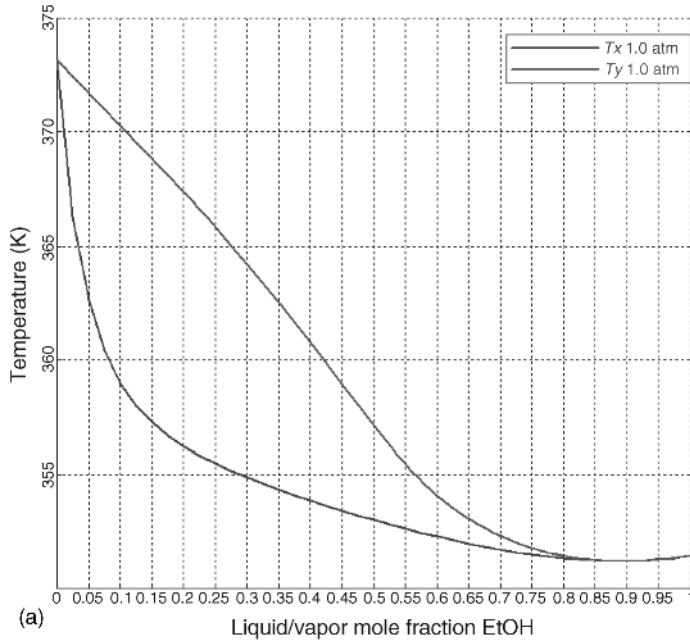


Figure 1.14 (a) T_{xy} diagram for ethanol/water. (b) Activity coefficient plot for ethanol/water. (c) xy plot for ethanol/water.

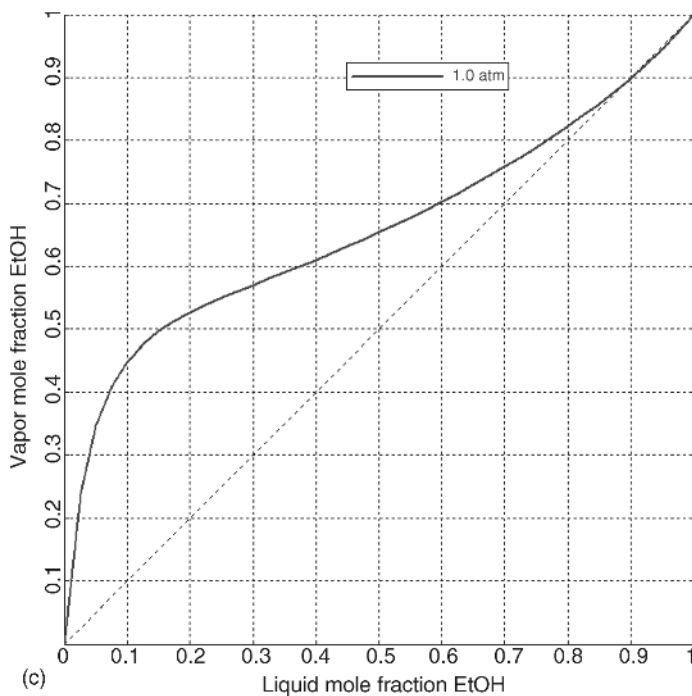


Figure 1.14 (Continued)

The software supplied in Aspen Plus provides a convenient method for calculating azeotropes. Go to *Tools* on the top tool bar, select *Conceptual Design* and *Azeotropic Search*. The window shown at the top of Figure 1.15 opens on which the components and pressure level are specified. The physical property package is set to be Uniquac. 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 90.0 mol% ethanol.

Let us now study a system in which there is more dissimilarity of the molecules by looking at the *n*-butanol/water system. The normal boiling point of *n*-butanol is 398 K, and that of water is 373 K, so water is the low boiler in this system. The azeotrope search results are shown in Figure 1.16, and the *Txy* diagram is shown in Figure 1.17. Notice that “*Vap-Liq-Liq*” is selected in the “*Phases*” under the “*Property Model*.”

The liquid-phase nonideality is so large that a heterogeneous azeotrope is formed. The molecules are so dissimilar that two liquid phases are formed. The composition of the vapor is 75.17 mol% water at 1 atm. The compositions of the two liquid phases that are in equilibrium with this vapor are 43.86 and 98.05 mol% water, respectively.

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 vapor stream is

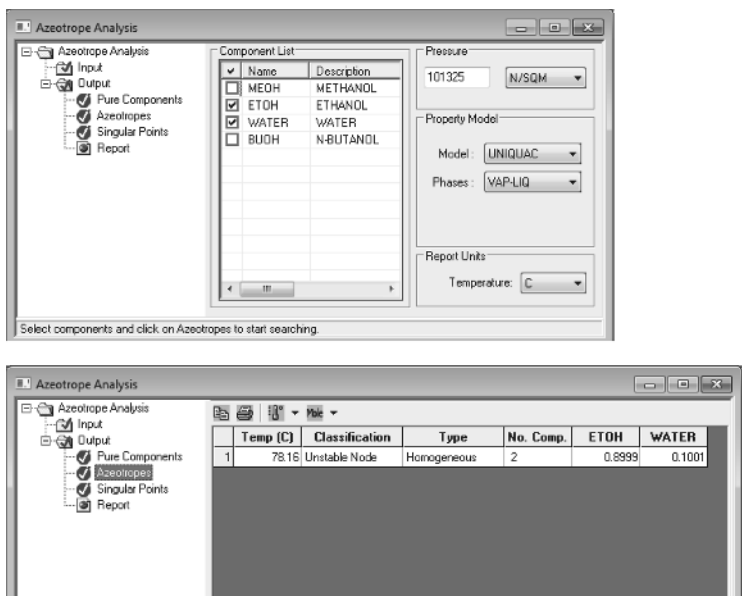


Figure 1.15 Azeotrope analysis: ethanol/water.

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

Figure 1.18 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 that 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

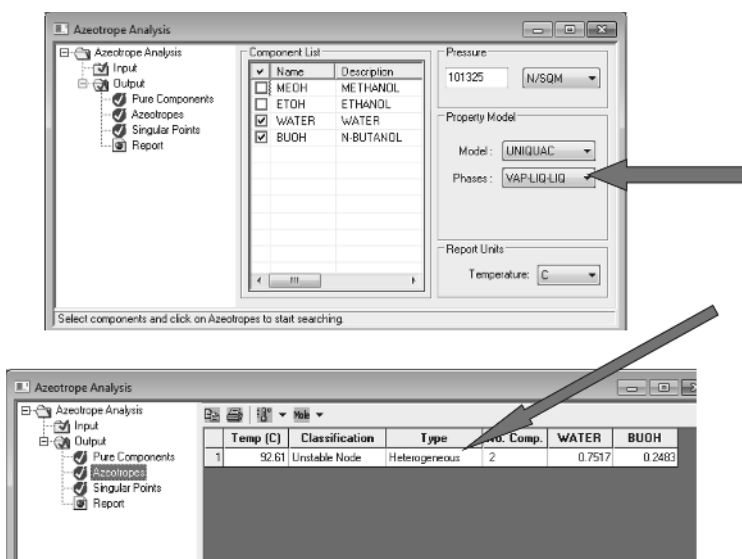


Figure 1.16 Azeotrope analysis: water/butanol.

Binary Analysis

Analysis type: Txy

Valid phases: Vapor-Liquid-Liquid

Components:
 Component 1: WATER
 Component 2: BUOH

Compositions:
 Basis: Mole fraction
 Component: WATER

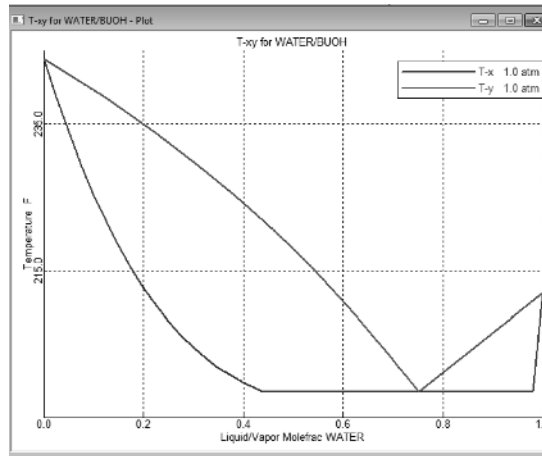
Pressure:
 Units: psia
 List of values: 14.69595

Property options:
 Property method: UNIQUAC
 Henry components:
 Chemistry ID:
 Simulation approach: True components

Buttons: Save As Form, Go, Cancel

Analysis is performed at the listed pressures.

(a)



(b)

Figure 1.17 (a) Txy analysis: water/butanol. (b) Txy diagram: water/butanol.

amount of liquid is 100 mol, and vapor is withdrawn at a rate of 1 mol per unit of time. Notice 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 1.19 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 in Aspen Plus. Click on *Tools* in the upper tool bar in the Aspen Plus window and select *Conceptual Design* and *Ternary Maps*. This opens the window shown in Figure 1.20 on which the three components and pressure 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 1.21. To generate a residue curve, right click the diagram and select *Add* and *Curve*. A cross-hair appears that can be

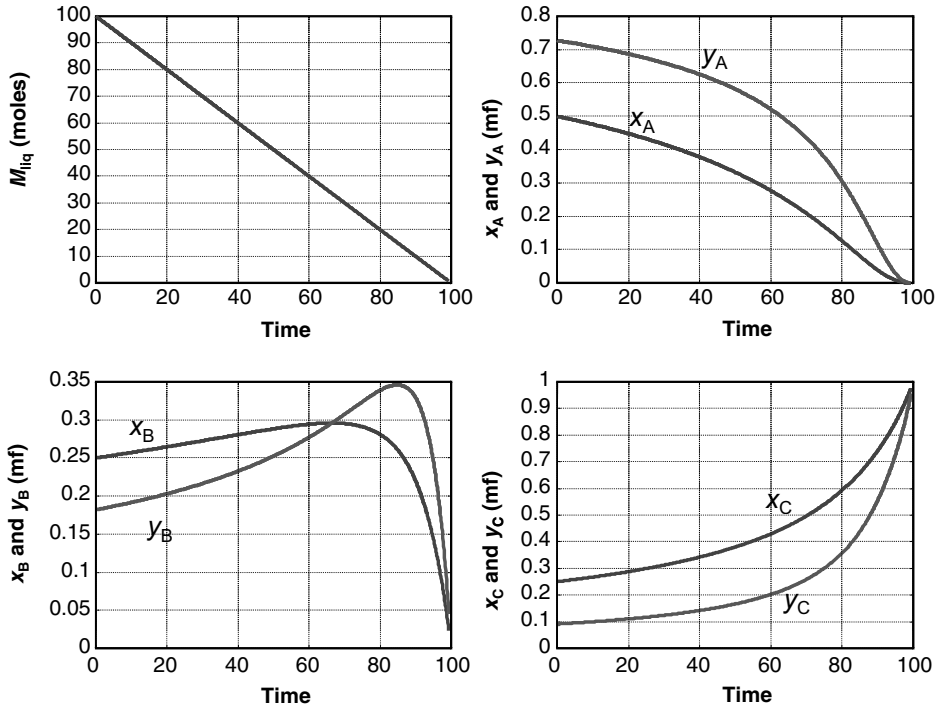


Figure 1.18 Generation of residue curves.

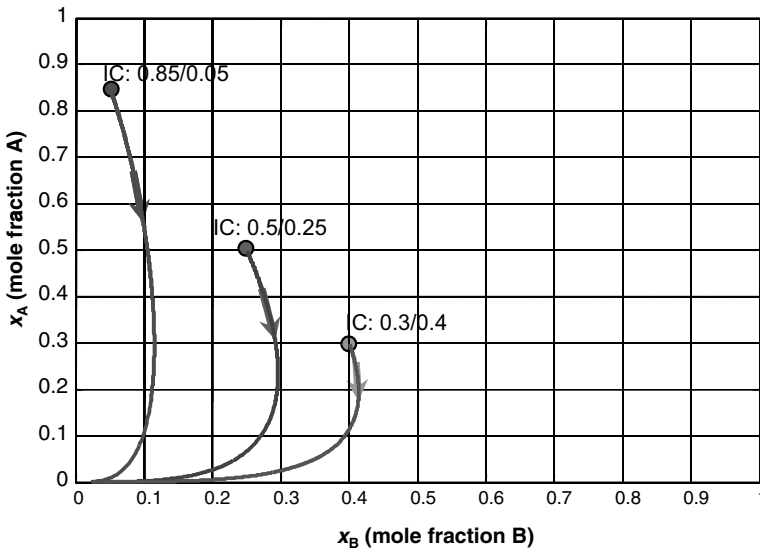


Figure 1.19 Residue curves starting from different initial conditions.

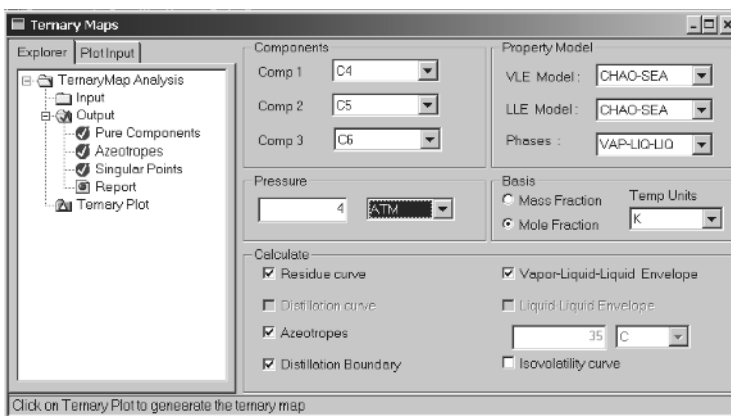


Figure 1.20 Setting up ternary maps.

moved to any location on the diagram. Clicking inserts a residue curve that passes through the selected point, as shown in Figure 1.22a. Repeating this procedure produces multiple residue curves shown in Figure 1.22b. Alternatively, the third button from the top on the right toolbar can be clicked. Then the cursor can be located at multiple points on the diagram, and right clicks will draw multiple residue curves.

Notice 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 to the top, and the heavy components go out at 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 components A and B . The rate of vapor withdrawal is V (moles per time).

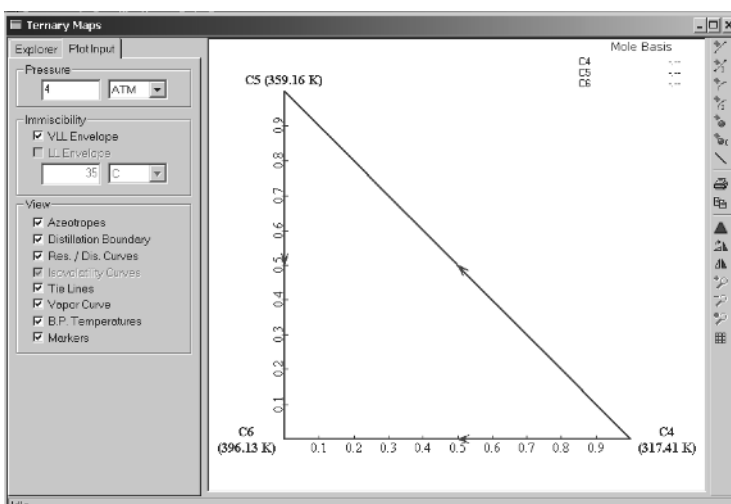
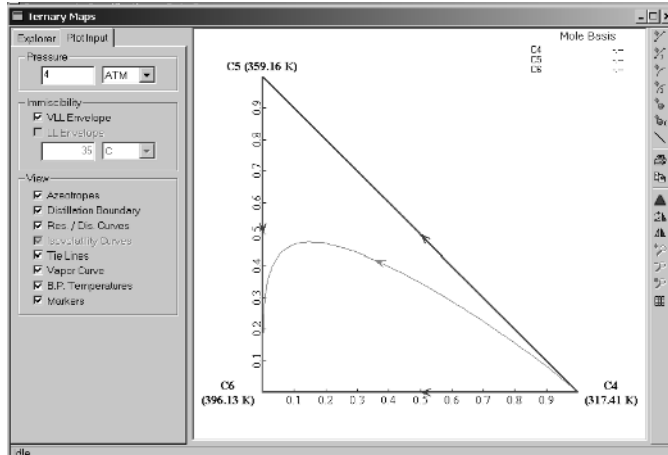
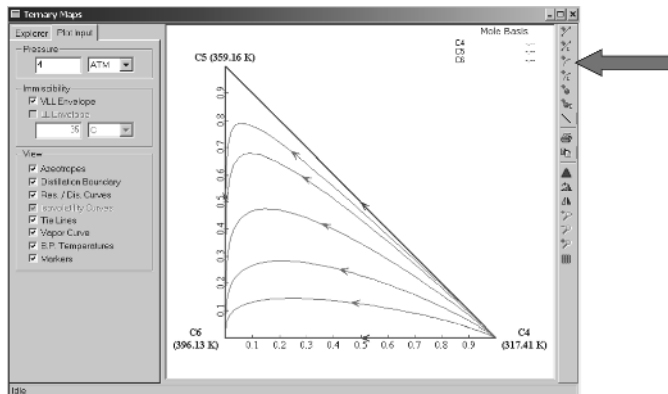


Figure 1.21 Ternary diagram for C4, C5, and C6.



(a)



(b)

Figure 1.22 (a) Adding a residue curve. (b) Several residue curves.

$$dM_{liq}/dt = -V$$

$$d(M_{liq}x_j)/dt = -Vy_j$$

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

$$M_{liq}(dx_j/dt) + x_j(dM_{liq}/dt) = -Vy_j$$

$$M_{liq}(dx_j/dt) + x_j(-V) = -Vy_j$$

$$(M_{liq}/V)(dx_j/dt) = x_j - y_j$$

$$dx_j/d\theta = x_j - y_j$$

The parameter θ is a dimensionless time variable. The last equation models how compositions change during the generation of a residue curve. As we develop below, a

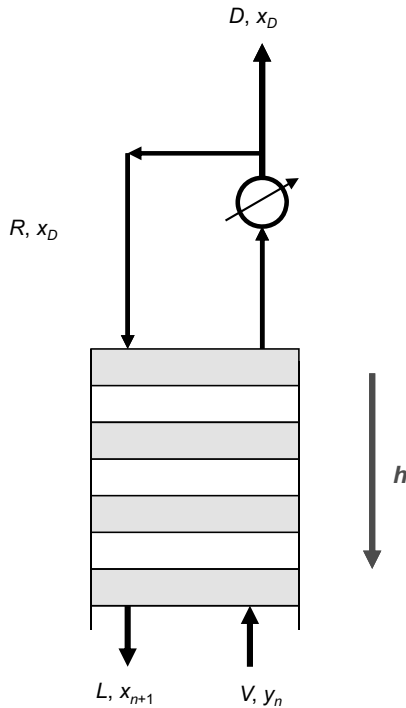


Figure 1.23 Distillation column.

similar equation describes the tray-to-tray liquid compositions in a distillation column under total reflux conditions. This relationship permits us to use residue curves to assess what separations are feasible or infeasible in a given system.

Consider the upper section of a distillation column shown in Figure 1.23. The column is cut at Tray n , at which the passing vapor and liquid streams have compositions y_{nj} and $x_{n+1,j}$ and flow rates are V_n and L_{n+1} . The distillate flow rate and composition are D and x_{Dj} , respectively. 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

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

Notice 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 DISTILLATION BOUNDARIES

The existence of azeotropes can introduce limits on the ability to separate components using distillation. These limitations are called distillation boundaries. They separate regions of feasible separations. Feed streams with compositions located in one region can produce certain products, while feed compositions in other regions will produce other products (different compositions of the distillate and bottoms streams).

To illustrate this phenomenon, let us start with a simple binary mixture. If there are no azeotropes, the xy diagram shows the VLE curve entirely above the 45° line, as shown in left graph in Figure 1.24. However, if there is a homogeneous minimum-boiling azeotrope as shown in Figure 1.25a, there is a distillation boundary at the azeotropic composition. The figure on the right shows that if the feed composition z_1 is lower than the azeotrope, the bottoms product will be mostly the *heavy-key* component, and the distillate will have a composition slightly lower than the azeotrope. On the other hand, if the feed composition is higher than the azeotrope (Fig. 1.25b), the bottoms product will be mostly the *light-key* component, and the distillate will have a composition slightly higher than the azeotrope.

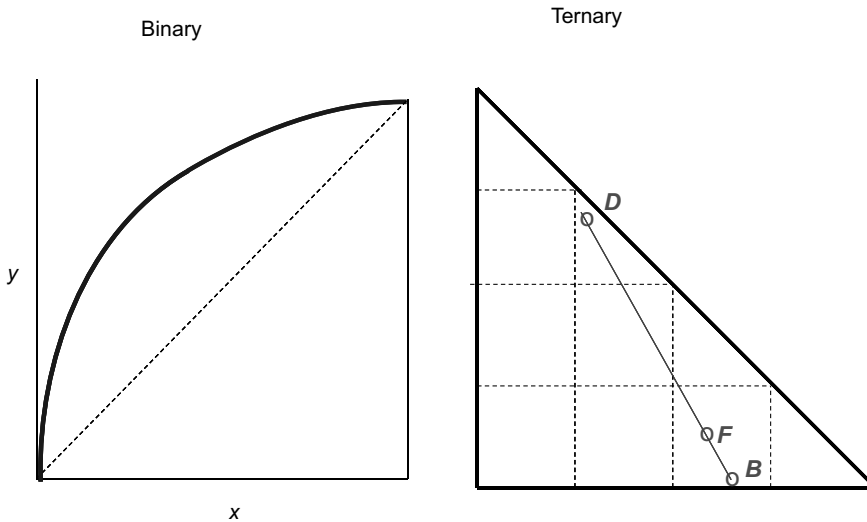


Figure 1.24 No distillation boundaries in ideal systems.

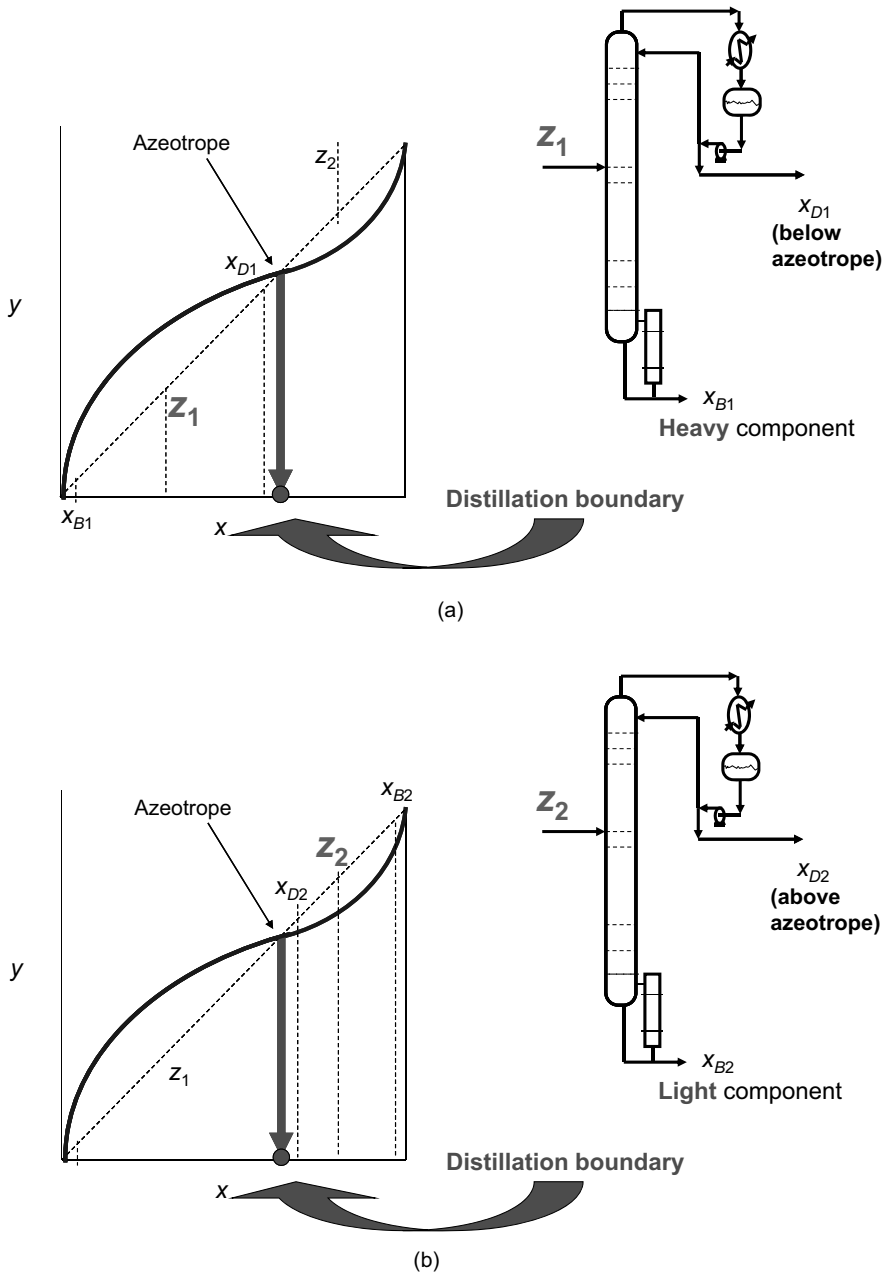


Figure 1.25 Distillation boundary in binary nonideal systems. (a) Feed composition z_1 less than azeotrope. (b) Feed composition z_2 greater than azeotrope.

Now, let us consider a ternary system. The ternary diagram of an ideal system shown in the right graph in Figure 1.24 displays no distillation boundaries. However, Figure 1.26 gives the ternary diagram for a nonideal system with two binary azeotropes. One is the A/B azeotrope and the other is the A/C azeotrope. A curve connecting the two azeotropes

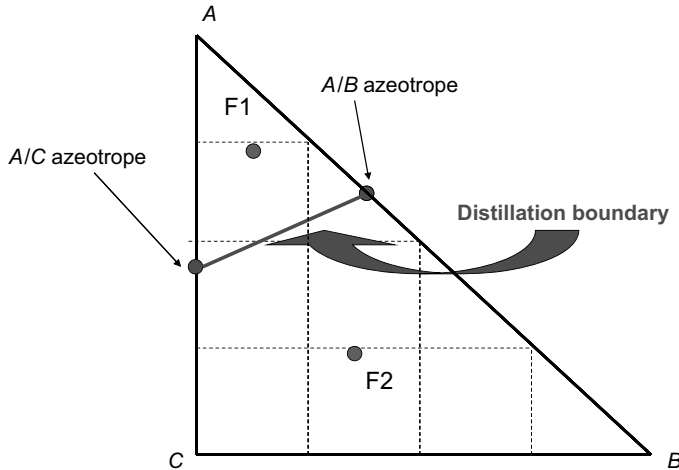


Figure 1.26 Distillation boundaries in ternary systems.

represents a distillation boundary. There are two regions in the ternary space. A feed stream located in the upper regions (F1) can produce products that lie only in this upper region. A feed stream located in the lower regions (F2) can produce products that lie only in this lower region.

The ternary system of methyl acetate, methanol, and water illustrates the occurrence of a distillation boundary. Figures 1.27 and 1.28 give the binary azeotropes of the system at 20 psia using NRTL physical properties. Figure 1.29 shows the ternary diagram with a distillation boundary.

A more complex system is shown in Figures 1.30 and 1.31. Ethanol, water, and benzene display three binary azeotropes and one ternary azeotrope. The resulting ternary diagram (Fig. 1.31) has three distillation boundaries that separate the ternary space into three regions.

We return to this complex system in Chapter 5 and develop a separation scheme for producing high-purity ethanol (upper corner in Fig. 1.31).

NRTL physical properties

Boiling points at 20 psia: MeOAc = 330.2 K
 MeOH = 337.7 K
 H₂O = 373.2 K

Binary azeotropes:

MeAc/MeOH: 64.5 mol% MeAc at 326.8 K
 MeOAc/H₂O: 95 mol% MeOAc at 330.1 K

Figure 1.27 Methyl acetate/methanol/water ternary.

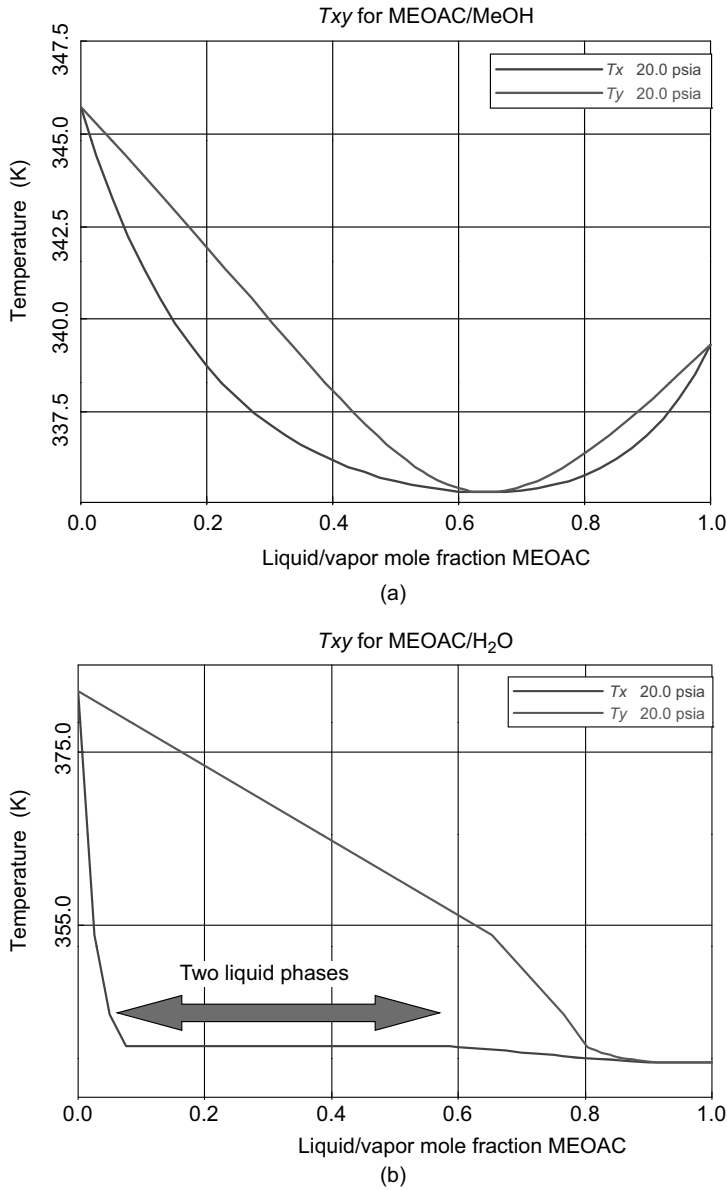


Figure 1.28 Binary azeotropes (NRTL). (a) Methyl acetate/methanol. (b) Methyl acetate/water.

1.10 CONCLUSIONS

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.

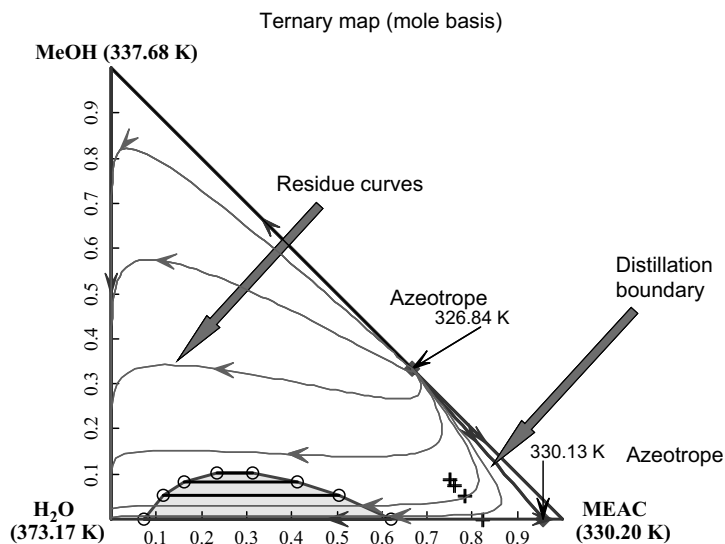


Figure 1.29 Methyl acetate/methanol/water ternary diagram.

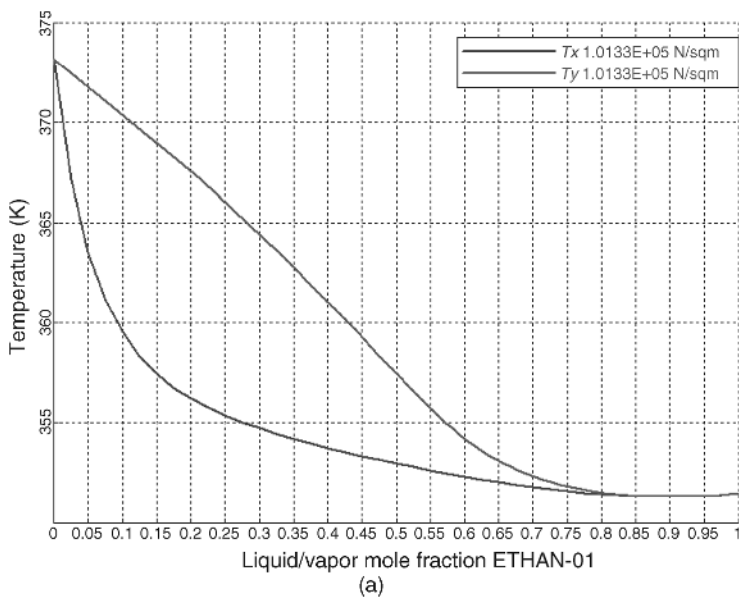


Figure 1.30 (a) T_{xy} diagram for ethanol/water. (b) T_{xy} diagram for ethanol/benzene.

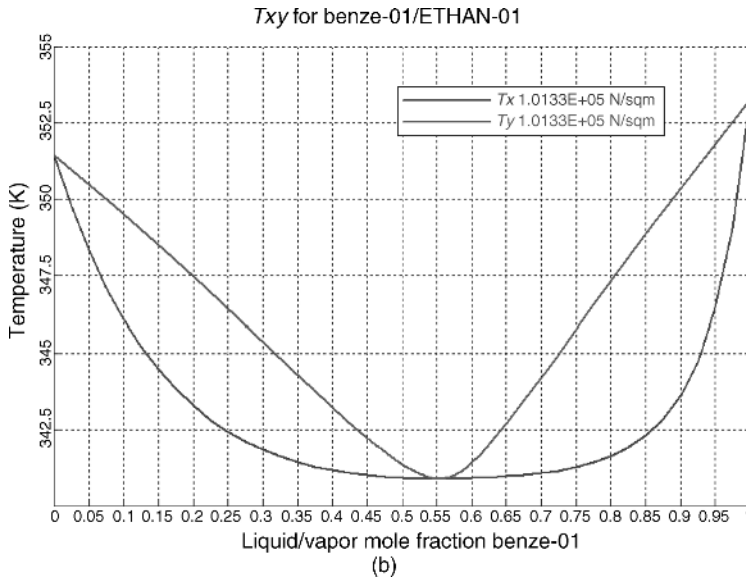


Figure 1.30 (Continued)

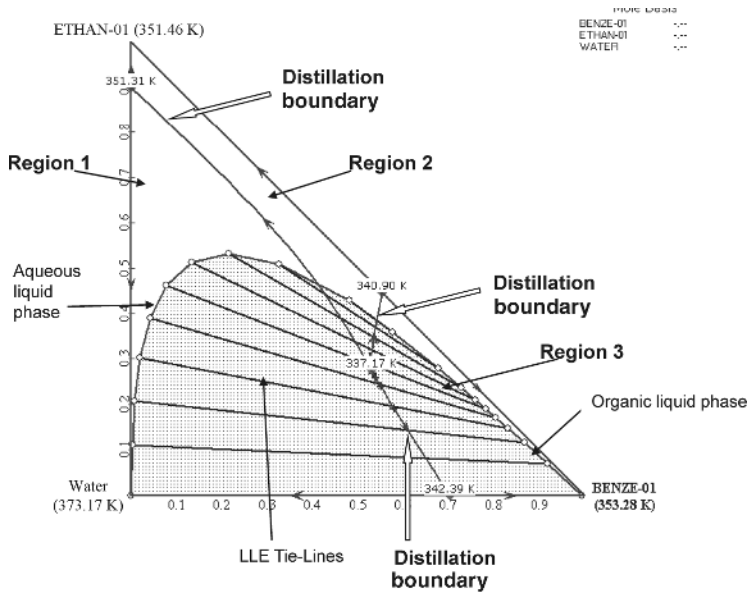


Figure 1.31 Ternary diagram.

REFERENCE

1. J. Gmehling et al., *Vapor-Liquid Equilibrium Data Collection*, DECHEMA, Frankfurt/Main, 1977.

