
DISTILLATION DESIGN AND CONTROL USING ASPENTM SIMULATION

WILLIAM L. LUYBEN

Lehigh University
Bethlehem, Pennsylvania

AIChE[®]

 **WILEY-
INTERSCIENCE**

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*Dedicated to the memory of the pioneers of
Lehigh Chemical Engineering:
Alan Foust, Len Wenzel, and Curt Clump*

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PREFACE

The rapid increase in the price of crude oil in recent years (as of 2005) and the resulting “sticker shock” at the gas pump have caused the scientific and engineering communities to finally understand that it is time for some reality checks on our priorities. Energy is the real problem that faces the world, and it will not be solved by the recent fads of biotechnology or nanotechnology. Energy consumption is the main producer of carbon dioxide, so it is directly linked with the problem of global warming.

A complete reassessment of our energy supply and consumption systems is required. Our terribly inefficient use of energy in all aspects of our modern society must be halted. We waste energy in our *transportation* system with poor-mileage SUVs and inadequate railroad systems. We waste energy in our *water* systems by using energy to produce potable water, and then flush most of it down the toilet. This loads up our *waste disposal* plants, which consume more energy. We waste energy in our *food* supply system by requiring large amounts of energy for fertilizer, herbicides, pesticides, tillage, and transporting and packaging our food for consumer convenience. The old farmers’ markets provided better food at lower cost and required much less energy.

One of the most important technologies in our energy supply system is distillation. Essentially all our transportation fuel goes through at least one distillation column on its way from crude oil to the gasoline pump. Large distillation columns called “pipestills” separate the crude into various petroleum fractions based on boiling points. Intermediate fractions go directly to gasoline. Heavy fractions are catalytically or thermally “cracked” to form more gasoline. Light fractions are combined to form more gasoline. Distillation is used in all of these operations.

Even when we begin to switch to renewable sources of energy such as biomass, the most likely transportation fuel will be methanol. The most likely process is the partial oxidation of biomass to produce synthesis gas (a mixture of hydrogen, carbon monoxide, and carbon dioxide) and the subsequent reaction of these components to produce methanol and water. Distillation to separate methanol from water is an important part of this process. Distillation is also used to produce the oxygen used in the partial oxidation reactor.

Therefore distillation is, and will remain in the twenty-first century, the premier separation method in the chemical and petroleum industries. Its importance is

unquestionable in helping to provide food, heat, shelter, clothing, and transportation in our modern society. It is involved in supplying much of our energy needs. The distillation columns in operation around the world number in the tens of thousands.

The analysis, design, operation, control, and optimization of distillation columns have been extensively studied for almost a century. Until the advent of computers, hand calculations and graphical methods were developed and widely applied in these studies. Since about 1950, analog and digital computer simulations have been used to solve many engineering problems. Distillation analysis involves iterative vapor–liquid phase equilibrium calculations and tray-to-tray component balances that are ideal for digital computation.

Initially most engineers wrote their own programs to solve both the nonlinear algebraic equations that describe the steady-state operation of a distillation column and the nonlinear ordinary differential equations that describe its dynamic behavior. Many chemical and petroleum companies developed their own in-house steady-state process simulation programs in which distillation was an important unit operation. Commercial *steady-state* simulators took over around the mid-1980s and now dominate the field.

Commercial *dynamic* simulators were developed quite a bit later. They had to wait for advancements in computer technology to provide the very fast computers required. The current state of the art is that both steady-state and dynamic simulations of distillation columns are widely used in industry and in universities.

My own technical experience has pretty much followed this history of distillation simulation. My practical experience started back in a high-school chemistry class in which we performed batch distillations. Next came an exposure to some distillation theory and running a pilot-scale batch distillation column as an undergraduate at Penn State, learning from Arthur Rose and “Black” Mike Cannon. Then there were 5 years of industrial experience in Exxon refineries as a technical service engineer on pipestills, vacuum columns, light-end units, and alkylation units, all of which used distillation extensively.

During this period the only use of computers that I was aware of was for solving linear programming problems associated with refinery planning and scheduling. It was not until returning to graduate school in 1960 that I personally started to use analog and digital computers. Bob Pigford taught us how to program a Bendix G12 digital computer, which used paper tape and had such limited memory that programs were severely restricted in length and memory requirements. Dave Lamb taught us analog simulation. Jack Gerster taught us distillation practice.

Next there were 4 years working in the Engineering Department of DuPont on process control problems, many of which involved distillation columns. Both analog and digital simulations were heavily used. A wealth of knowledge was available from a stable of outstanding engineers: Page Buckley, Joe Coughlin, J. B. Jones, Neal O’Brien, and Tom Keane, to mention only a few.

Finally, there have been over 35 years of teaching and research at Lehigh in which many undergraduate and graduate students have used simulations of distillation columns in isolation and in plantwide environments to learn basic distillation principles and to develop effective control structures for a variety of distillation column configurations. Both homegrown and commercial simulators have been used in graduate research and in the undergraduate senior design course.

The purpose of this book is to try to capture some of this extensive experience with distillation design and control so that it is available to students and young engineers

when they face problems with distillation columns. This book covers much more than just the mechanics of using a simulator. It uses simulation to guide in developing the optimum economic steady-state design of distillation systems, using simple and practical approaches. Then it uses simulation to develop effective control structures for dynamic control. Questions are addressed as to whether to use single-end control or dual-composition control, where to locate temperature control trays, and how excess degrees of freedom should be fixed.

There is no claim that the material is all new. The steady-state methods are discussed in most design textbooks. Most of the dynamic material is scattered around in a number of papers and books. What is claimed is that this book pulls this material together in a coordinated, easily accessible way. Another unique feature is the combination of design and control of distillation columns in a single book.

There are three steps in developing a process design. The first is “conceptual design,” in which simple approximate methods are used to develop a preliminary flowsheet. This step for distillation systems is covered very thoroughly in another textbook.¹ The next step is *preliminary design*, in which rigorous simulation methods are used to evaluate both steady-state and dynamic performance of the proposed flowsheet. The final step is “detailed design,” in which the hardware is specified in great detail, with specifics such as types of trays, number of sieve tray holes, feed and reflux piping, pumps, heat exchanger areas, and valve sizes. This book deals with the second stage, preliminary design.

The subject of distillation simulation is a very broad one, which would require many volumes to cover comprehensively. The resulting encyclopedia-like books would be too formidable for a beginning engineer to try to tackle. Therefore this book is restricted in its scope to only those aspects that I have found to be the most fundamental and the most useful. Only continuous distillation columns are considered. The area of batch distillation is very extensive and should be dealt with in another book. Only staged columns are considered. They have been successfully applied for many years. Rate-based models are fundamentally more rigorous, but they require that more parameters be known or estimated.

Only rigorous simulations are used in this book. The book by Doherty and Malone is highly recommended for a detailed coverage of approximate methods for conceptual steady-state design of distillation systems.

I hope that the reader finds this book useful and readable. It is a labor of love that is aimed at taking some of the mystery and magic out of designing and operating a distillation column.

WILLIAM L. LUYBEN

¹M. F. Doherty and M. F. Malone, *Conceptual Design of Distillation Systems*, McGraw-Hill, 2001.

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

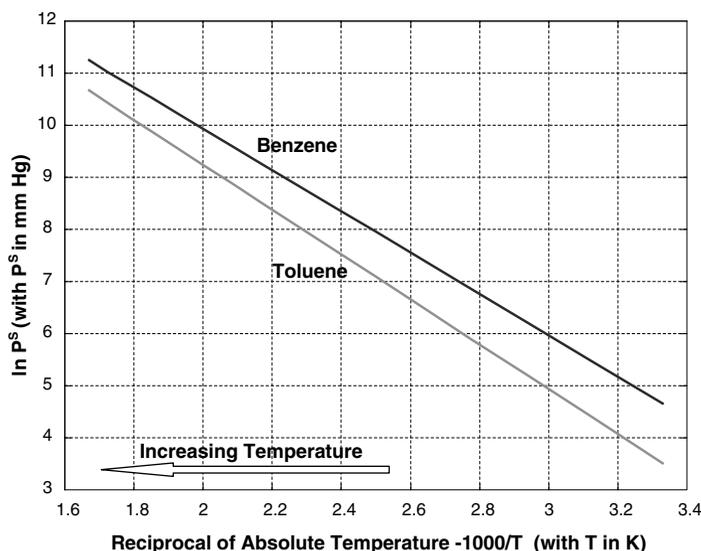


Figure 1.1 Vapor pressures of pure benzene and toluene.

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.

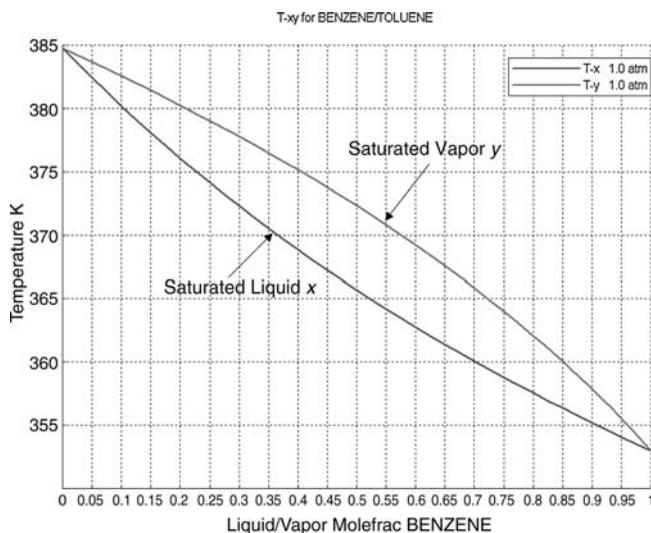


Figure 1.2 Txy diagram for benzene and toluene at 1 atm.

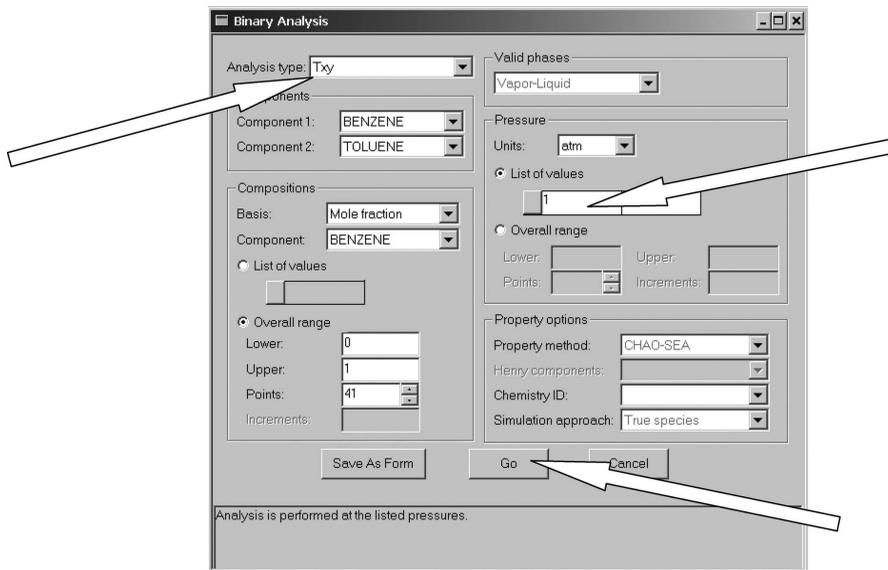


Figure 1.3 Specifying Txy diagram parameters.

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.

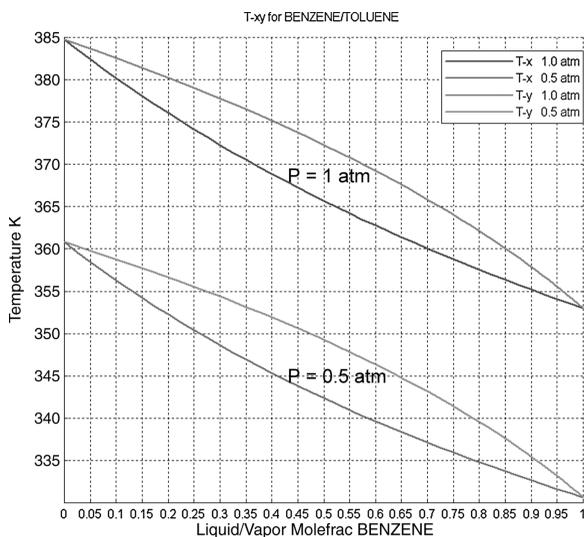


Figure 1.4 Txy diagrams at two pressures.

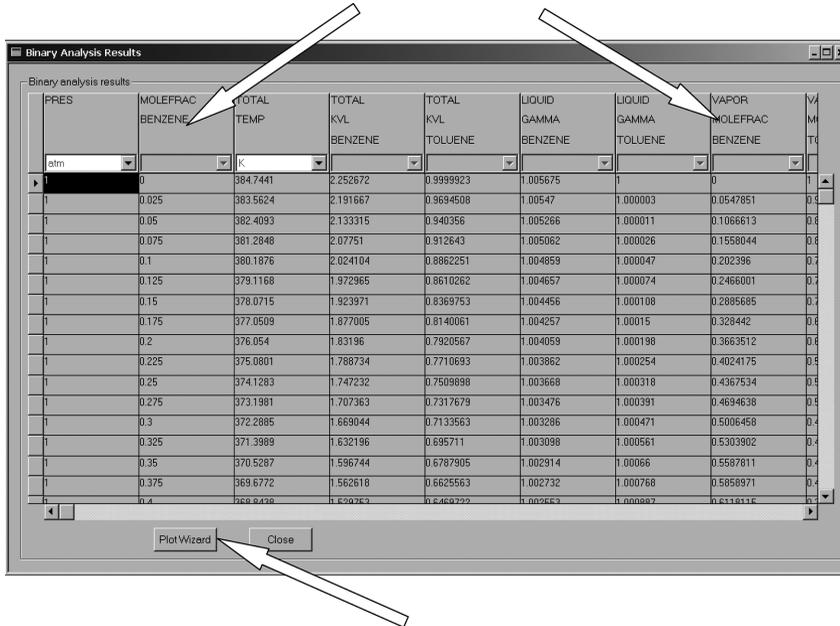


Figure 1.5 Using Plot Wizard to generate xy diagram.

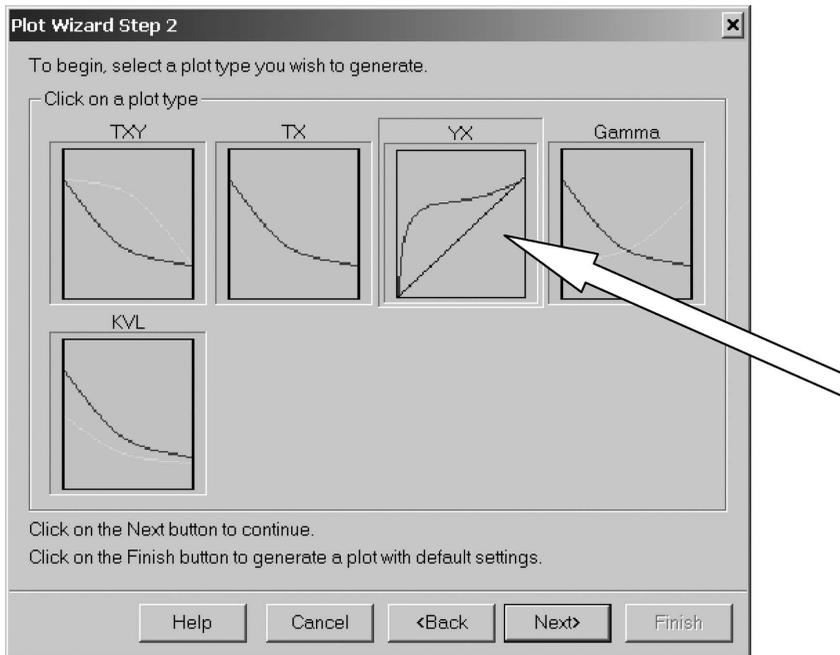


Figure 1.6 Using Plot Wizard to generate xy diagram.

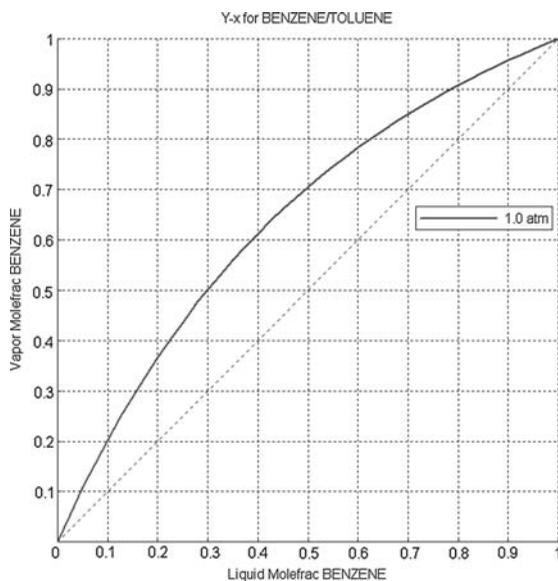


Figure 1.7 xy diagram for benzene/toluene.

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.

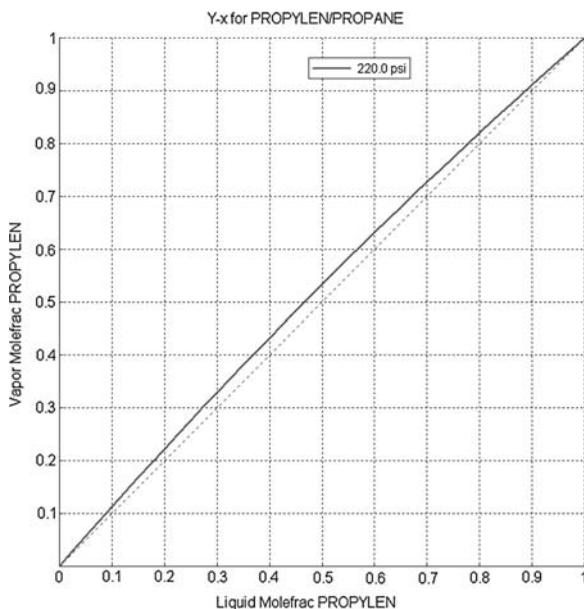


Figure 1.8 xy diagram for propylene/propane.

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.

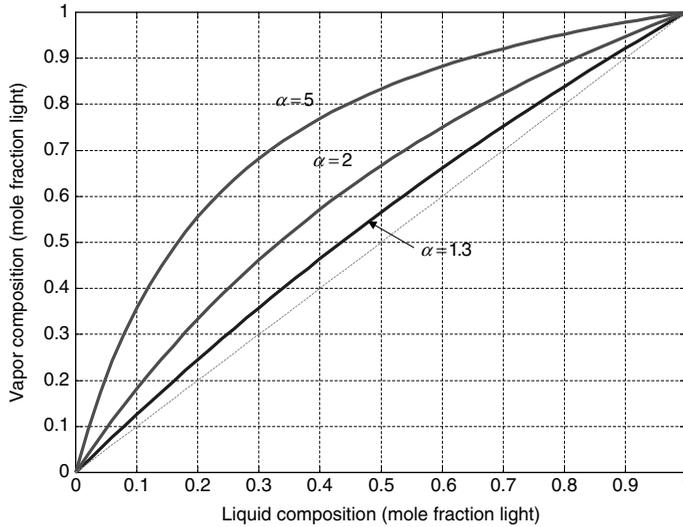


Figure 1.9 xy curves for relative volatilities of 1.3, 2, and 5.

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:

$$F = D + B$$

$$Fz_1 = Dx_{D1} + Bx_{B1}$$

$$Fz_2 = Dx_{D2} + Bx_{B2}$$

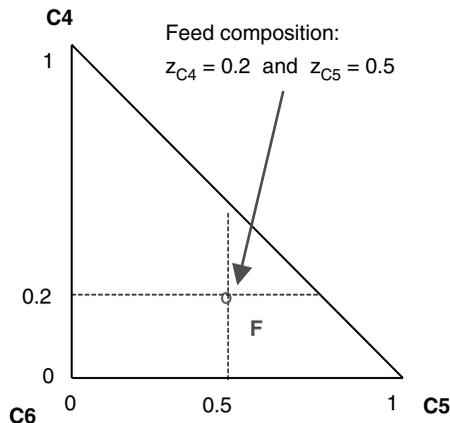


Figure 1.10 Ternary diagram.

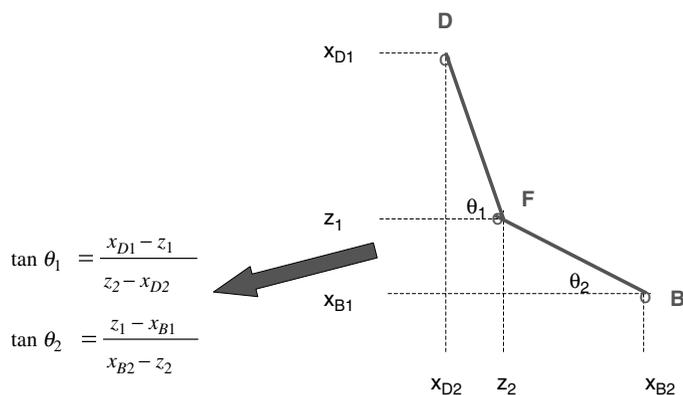


Figure 1.12 Proof of collinearity.

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 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.

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.

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

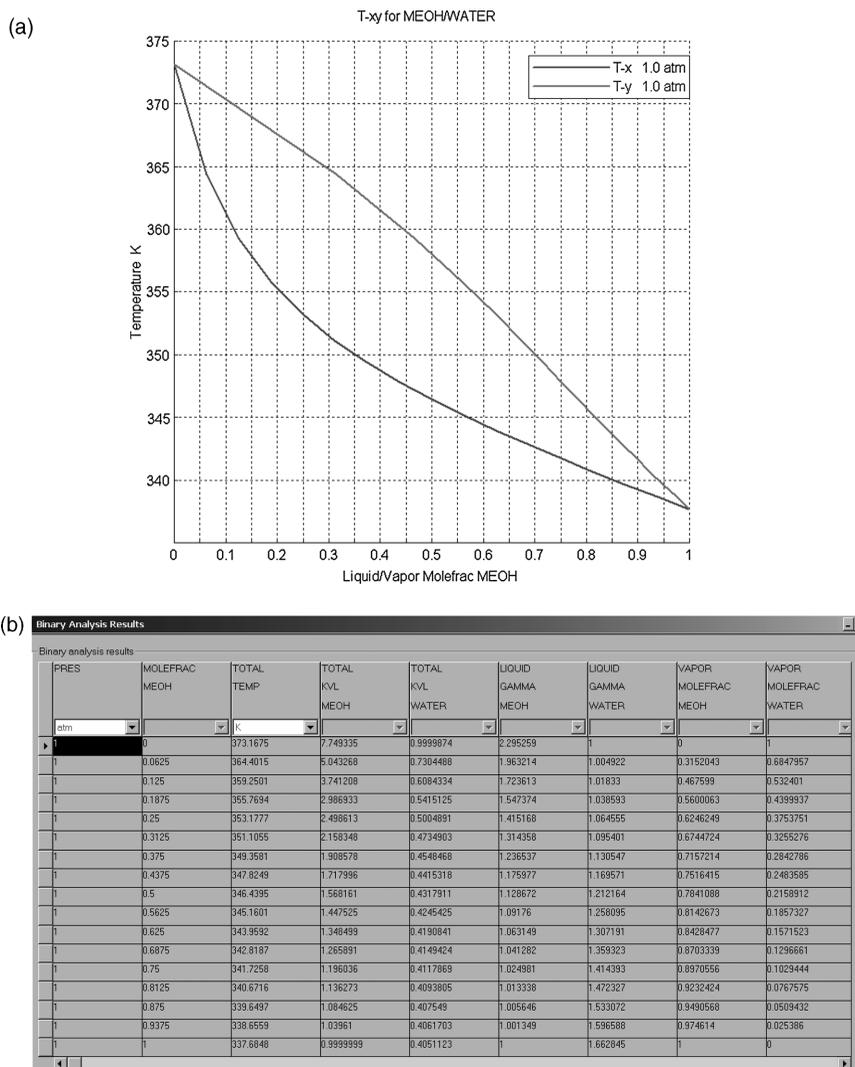


Figure 1.13 (a) Txy diagram for methanol/water; (b) activity coefficients for methanol/water; (c) activity coefficient plot for methanol/water.

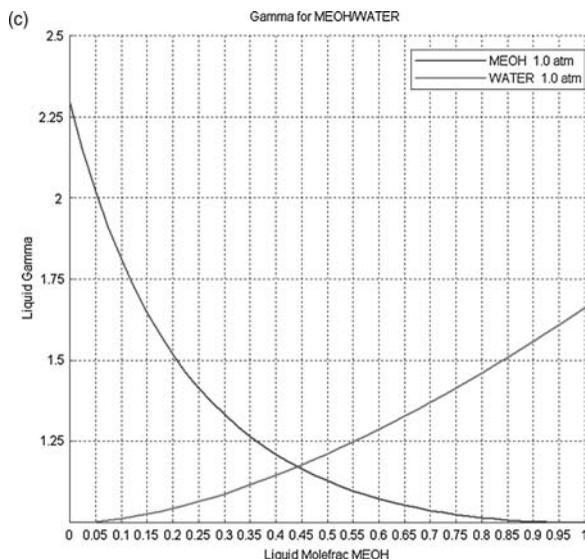


Figure 1.13 Continued.

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.

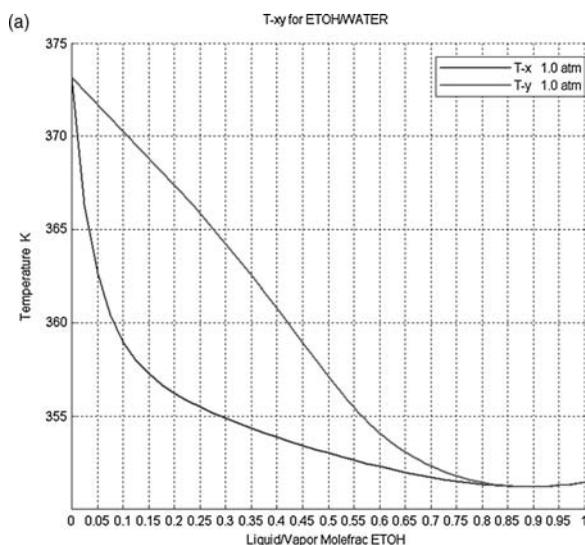


Figure 1.14 Txy diagram for ethanol/water (a), activity coefficient plot (b), and xy plot (c) for ethanol/water.