Chapter 10

Vapor/Liquid Equilibrium: Introduction

Preceding chapters have dealt largely with pure substances or with constant-composition mixtures. e.g., air. However, composition changes are the desired outcome, not only of chemical reactions, but of a number of industrially important mass-transfer operations. Thus composition becomes a primary variable in the remaining chapters of this text. Processes such as distillation, absorption, and extraction bring phases of different composition into contact, and when the phases are not in equilibrium, mass transfer between the phases alters their compositions. Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium. Thus, for quantitative treatment of mass transfer the equilibrium T, P, and phase compositions must be known.

The most commonly encountered coexisting phases in industrial practice are vapor and liquid, although liquid/liquid, vaporlsolid, and liquid/solid systems are also found. In this chapter we first discuss the nature of equilibrium, and then consider two rules that give the number of independent variables required to determine equilibrium states. There follows in Sec. 10.3 a qualitative discussion of vapor/liquid phase behavior. In Sec. 10.4 we introduce the two simplest formulations that allow calculation of temperatures, pressures, and phase compositions for systems in vaporlliquid equilibrium. The first, known as Raoult's law, is valid only for systems at low to moderate pressures and in general only for systems comprised of chemically similar species. The second, known as Henry's law, is valid for any species present at low concentration, but as presented here is also limited to systems at low to moderate pressures. A modification of Raoult's law that removes the restriction to chemically similar species is treated in Sec. 10.5. Finally in Sec. 10.6 calculations based on equilibrium ratios or K-values are considered. The treatment of vapor/liquid equilibrium is developed further in Chaps. 12 and 14.

10.1 THE NATURE OF EQUILIBRIUM

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy. For example, in the reboiler for a distillation column, equilibrium between vapor and

liquid phases is commonly assumed. For finite vaporization rates this is an approximation, but it does not introduce significant error into engineering calculations.

An isolated system consisting of liquid and vapor phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium. Nevertheless, at the microscopic level, conditions are not static. The molecules comprising a phase at a given instant are not the same molecules that later occupy the same phase. Molecules with sufficiently high velocities near the interface overcome surface forces and pass into the other phase. However, the average rate of passage of molecules is the same in both directions, and no net interphase transfer of material occurs.

Measures of Composition

The three most common measures of composition are mass fraction, mole fraction, and molar concentration. Mass or mole fraction is defined as the ratio of the mass or number of moles of a particular chemical species in a mixture or solution to the total mass or number of moles of the mixture or solution:

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \qquad \text{or} \qquad x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

Molar concentration is defined as the ratio of the mole fraction of a particular chemical species in a mixture or solution to its molar volume:

$$C_i \equiv \frac{x_i}{V}$$

This quantity has units of moles of i per unit volume. For flow processes convenience suggests its expression as a ratio of rates. Multiplying and dividing by molar flow rate ri gives:

$$C_i = \frac{\dot{n}_i}{q}$$

where $\dot{n}_i$ is molar flow rate of species i, and q is volumetric flow rate.

The molar mass of a mixture or solution is, by definition, the mole-fraction-weighted sum of the molar masses of all species present:

$$M \equiv \sum_i x_i M_i$$

10.2   THE PHASE RULE. DUHEM'S THEOREM

The phase rule for nonreacting systems, presented without proof in Sec. 2.7, results from application of a rule of algebra. Thus, the number of variables that may be independently fixed in a system at equilibrium is the difference between the total number of variables that characterize the intensive state of the system and the number of independent equations that can be written connecting the variables.

The *intensive* state of a PVT system containing N chemical species and π phases in equilibrium is characterized by the intensive variables, temperature T, pressure P, and

N − 1 mole fractions[1] for each phase. These are the phase-rule variables, and their number is $2 + (N − 1)(\pi)$. The masses of the phases are not phase-rule variables, because they have no influence on the intensive state of the system.

As will become clear later in this chapter, an independent phase-equilibrium equation may be written connecting intensive variables for each of the N species for each pair of phases present. Thus, the number of independent phase-equilibrium equations is $(\pi − 1)(N)$. The difference between the number of phase-rule variables and the number of independent equations connecting them is the number of variables that may be independently fixed. Called the degrees of freedom of the system **F**, the number is:

$$F = 2 + (N − 1)(\pi) − (\pi − 1)(N)$$

Upon reduction, this becomes the phase rule:

$$\boxed{F = 2 − \pi + N} \tag{2.7}$$

Duhem's theorem is another rule, similar to the phase rule, but less celebrated. It applies to closed systems at equilibrium for which the extensive state as well as the intensive state of the system is fixed. The state of such a system is said to be *completely determined,* and is characterized not only by the $2 + (N − 1)\pi$ intensive phase-rule variables but also by the π extensive variables represented by the masses (or mole numbers) of the phases. Thus the total number of variables is:

$$2 + (N − 1)\pi + \pi = 2 + N\pi$$

If the system is closed and formed from specified amounts of the chemical species present, then a material-balance equation can be written for each of the N chemical species. These in addition to the $(\pi − 1)N$ phase-equilibrium equations provide a total number of independent equations equal to:

$$(\pi − 1)N + N = \pi N$$

The difference between the number of variables and the number of equations is therefore:

$$2 + N\pi − \pi N = 2$$

On the basis of this result, Duhem's theorem is stated as follows:

> **For any closed system formed initially from given masses of pre-scribed chemical species, the equilibrium state is completely deter-mined when any two independent variables are fixed.**

The two independent variables subject to specification may in general be either intensive or extensive. However, the number of *independent intensive* variables is given by the phase rule. Thus when $F = 1$, at least one of the two variables must be extensive, and when $F = 0$, both must be extensive.

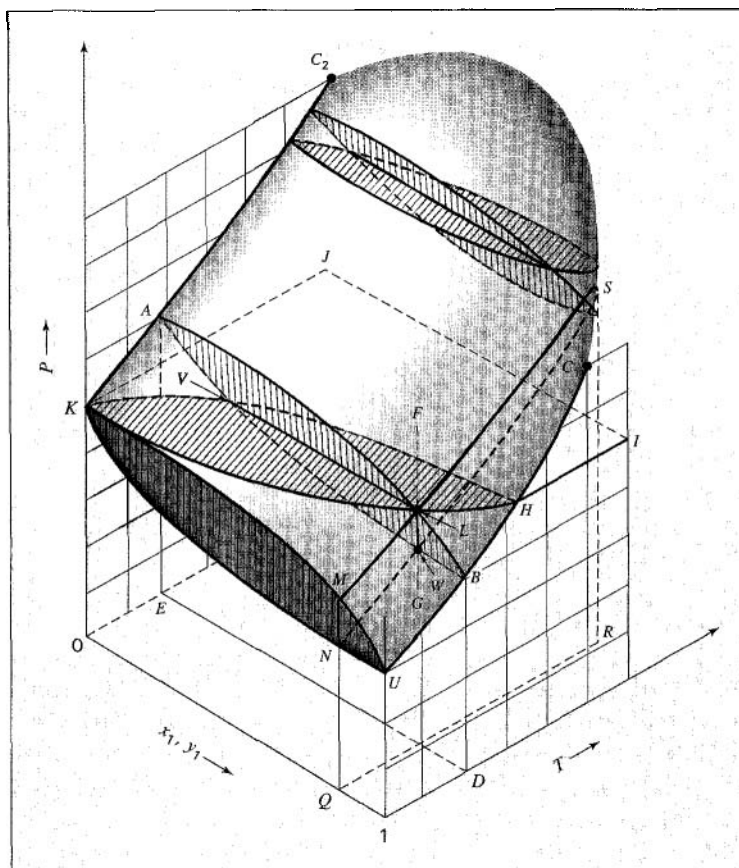[1] Only N − 1 mole fractions are required, because $\sum_i x_i = 1$.

Figure 10.1 $PTxy$ diagram for vapor/liquid equilibrium

10.3 VLE: QUALITATIVE BEHAVIOR

Vapor/liquid equilibrium (VLE) is the state of coexistence of liquid and vapor phases. In this qualitative discussion, we limit consideration to systems comprised of two chemical species, because systems of greater complexity cannot be adequately represented graphically.

When $N = 2$, the phase rule becomes $F = 4 - n$. Since there must be at least one phase ($n = 1$), the maximum number of phase-rule variables which must be specified to fix the intensive state of the system is *three:* namely, P, T, and one mole (or mass) fraction. All equilibrium states of the system can therefore be represented in three-dimensional P-T-composition space. Within this space, the states of *pairs* of phases coexisting at equilibrium ($F = 4 - 2 = 2$) define surfaces. A schematic three-dimensional diagram illustrating these surfaces for VLE is shown in Fig. 10.1.

This figure shows schematically the P-T-composition surfaces which contain the equilibrium states of saturated vapor and saturated liquid for a binary system. The under surface contains the saturated-vapor states; it is the P-T-y_1 surface. The upper surface contains the saturated-liquid states; it is the P-T-x_1 surface. These surfaces intersect along the lines $UBHC_1$

and KAC_2, which represent the vapor pressure-vs.-T curves for pure species 1 and 2. More-over, the under and upper surfaces form a continuous rounded surface across the top of the diagram between C_1 and C_2, the critical points of pure species 1 and 2; the critical points of the various mixtures of the two species lie along a line on the rounded edge of the surface between C_1 and C_2. This critical locus is defined by the points at which vapor and liquid phases in equilibrium become identical. Further discussion of the critical region is given later.

The subcooled-liquid region lies above the upper surface of Fig. 10.1; the superheated-vapor region lies below the under surface. The interior space between the two surfaces is the region of coexistence of both liquid and vapor phases. If one starts with a liquid at F and reduces the pressure at constant temperature and composition along vertical line FG, the first bubble of vapor appears at point L, which lies on the upper surface. Thus, L is a bubblepoint, and the upper surface is the bubblepoint surface. The state of the vapor bubble in equilibrium with the liquid at L must be represented by a point on the under surface at the temperature and pressure of L. This point is indicated by V. Line VL is an example of a tie line, which connects points representing phases in equilibrium.

As the pressure is further reduced along line FG, more and more liquid vaporizes until at W the process is complete. Thus W lies on the under surface and represents a state of saturated vapor having the mixture composition. Since W is the point at which the last drops of liquid (dew) disappear, it is a dewpoint, and the lower surface is the dewpoint surface. Continued reduction of pressure merely leads into the superheated vapor region.

Because of the complexity of Fig. 10.1, the detailed characteristics of binary VLE are usually depicted by two-dimensional graphs that display what is seen on various planes that cut the three-dimensional diagram. The three principal planes, each perpendicular to one of the coordinate axes, are illustrated in Fig. 10.1. Thus a vertical plane perpendicular to the temperature axis is outlined as ALBDEA. The lines on this plane form a P-x_1-y_1 phase diagram at constant T. If the lines from several such planes are projected on a single parallel plane, a diagram like Fig. 10.2(a) is obtained. It shows P-x_1-y_1 plots for three different temperatures. The one for T_a represents the section of Fig. 10.1 indicated by ALBDEA. The horizontal lines are tie lines connecting the compositions of phases in equilibrium. The temperature T_b lies between the two pure-species critical temperatures identified by C_1 and C_2 in Fig. 10.1, and temperature T_d is above both critical temperatures. The curves for these two temperatures therefore do not extend all the way across the diagram. However, the first passes through one mixture critical point, and the second through two such points. All three of these critical points are denoted by the letter C. Each is a tangent point at which a horizontal line touches the curve. This is so because all tie lines connecting phases in equilibrium are horizontal, and the tie line connecting identical phases (the definition of a critical point) must therefore be the last such line to cut the diagram.

A horizontal plane passed through Fig. 10.1 perpendicular to the P axis is identified by HIJKLH. Viewed from the top, the lines on this plane represent a T-x_1-y_1 diagram. When lines for several pressures are projected on a parallel plane, the resulting diagram appears as in Fig. 10.2(b). This figure is analogous to Fig. 10.2(a), except that it represents values for three constant pressures, P_a, P_b, and P_d.

Other possible plots are vapor mole fraction y_1 vs. liquid mole fraction x_1 for either the constant-T conditions of Fig. 10.2(a) or the constant-P conditions of Fig. 10.2(b).

The third plane identified in Fig. 10.1, vertical and perpendicular to the composition axis, is indicated by MNQRSLM. When projected on a parallel plane, the lines from several
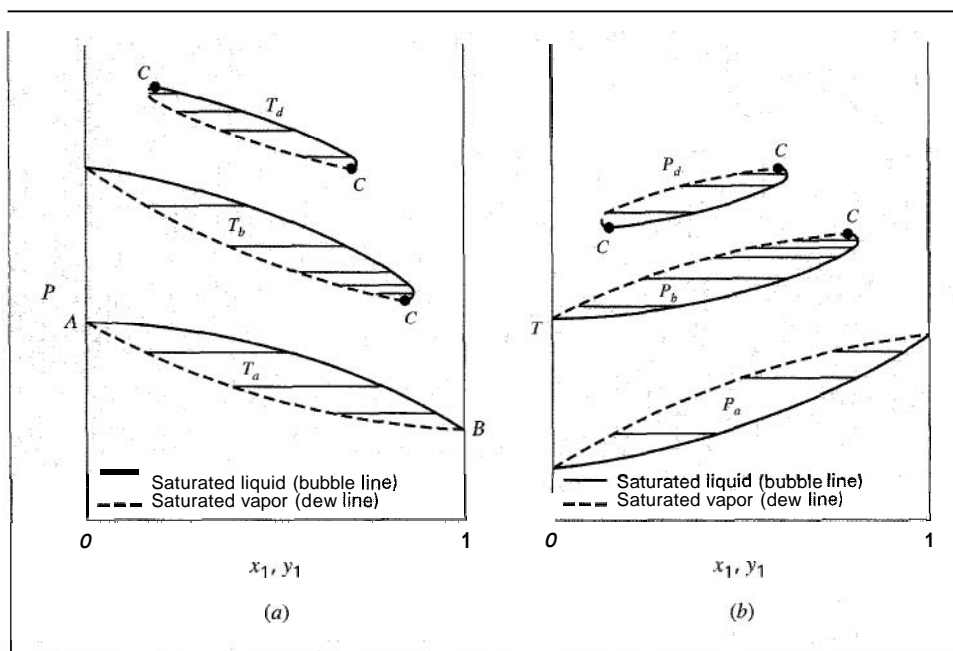
Figure *10.2* (a) Pxy diagram for three temperatures. (b) **Txy** diagram for three pressures

planes present a diagram such as that shown by Fig. 10.3. This is the **P-T** diagram; lines UC_1 and KC_2 are vapor-pressure curves for the pure species, identified by the same letters as in Fig. 10.1. Each interior loop represents the **P-T** behavior of saturated liquid and of saturated vapor for a *mixture of fixed composition;* the different loops are for different compositions. Clearly, the **P-T** relation for saturated liquid is different from that for saturated vapor of the same composition. This is in contrast with the behavior of a pure species, for which the bubble and dew lines coincide. At points A and B in Fig. 10.3 saturated-liquid and saturated-vapor lines intersect. At such points a saturated liquid of one composition and a saturated vapor of another composition have the same T and **P ,**and the two phases are therefore in equilibrium. The tie lines connecting the coinciding points at A and at B are perpendicular to the P-T plane, as illustrated by the tie line VL in Fig. 10.1.

The critical point of a binary mixture occurs where the nose of a loop in Fig. 10.3 is tangent to the envelope curve. Put another way, the envelope curve is the critical locus. One can verify this by considering two closely adjacent loops and noting what happens to the point of intersection as their separation becomes infinitesimal. Figure 10.3 illustrates that the location of the critical point on the nose of the loop varies with composition. For a pure species the critical point is the highest temperature and highest pressure at which vapor and liquid phases can coexist, but for a mixture it is in general neither. Therefore under certain conditions a condensation process occurs as the result of a *reduction* in pressure.

Consider the enlarged nose section of a single P-T loop shown in Fig.10.4. The critical point is at C. The points of maximum pressure and maximum temperature are identified as M_P and M_T. The interior dashed curves indicate the fraction of the overall system that is liquid
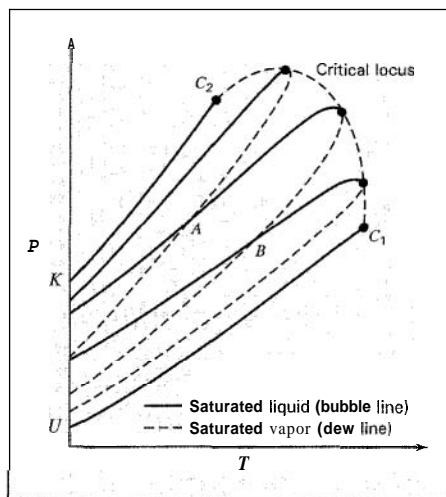
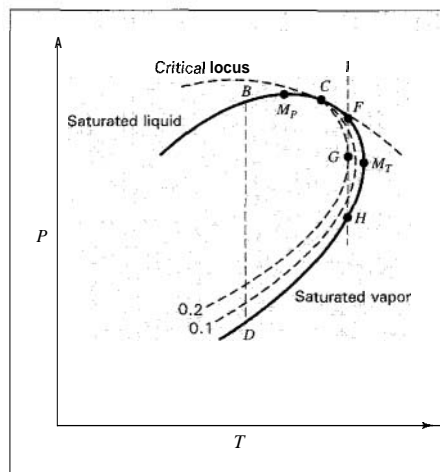**Figure 10.3** PT diagram for several compositions

Figure 10.4 Portion of a PT diagram in the critical region

in a two-phase mixture of liquid and vapor. To the left of the critical point C a reduction in pressure along a line such as BD is accompanied by vaporization of liquid from bubblepoint to dewpoint, as would be expected. However, if the original condition corresponds to point F, a state of saturated vapor, liquefaction occurs upon reduction of the pressure and reaches a maximum at point G, after which vaporization takes place until the dewpoint is reached at point H. This phenomenon is called retrograde condensation. It can be important in the operation of deep natural-gas wells where the pressure and temperature in the underground formation are at conditions represented by point F. If the pressure at the wellhead is that of point G, considerable liquefaction of the product stream is accomplished along with partial separation of the heavier species of the mixture. Within the underground formation itself, the pressure tends to drop as the gas supply is depleted. If not prevented, this leads to the formation of a liquid phase and a consequent reduction in the production of the well. Repressuring is therefore a common practice; i.e., lean gas (gas from which the heavier species have been removed) is returned to the underground reservoir to maintain an elevated pressure.

A P-T diagram for the ethane(1)/n-heptane(2) system is shown in Fig. 10.5, and a y_1-x_1 diagram for several pressures for the same system appears in Fig. 10.6. According to convention, one plots as y_1 and x_1 the mole fractions of the more volatile species in the mixture. The maximum and minimum concentrations of the more volatile species obtainable by distillation at a given pressure are indicated by the points of intersection of the appropriate y_1-x_1 curve with the diagonal, for at these points the vapor and liquid have the same composition. They are in fact mixture critical points, unless $y_1 = x_1 = 0$ or $y_1 = x_1 = 1$. Point A in Fig. 10.6 represents the composition of the vapor and liquid phases at the maximum pressure at which the phases can coexist in the ethaneln-heptane system. The composition is about 77 mol-% ethane and the pressure is about 87.1 bar. The corresponding point on Fig. 10.5 is labeled M. A complete set of consistent phase diagrams for this system has been prepared by Barr-David.[2]

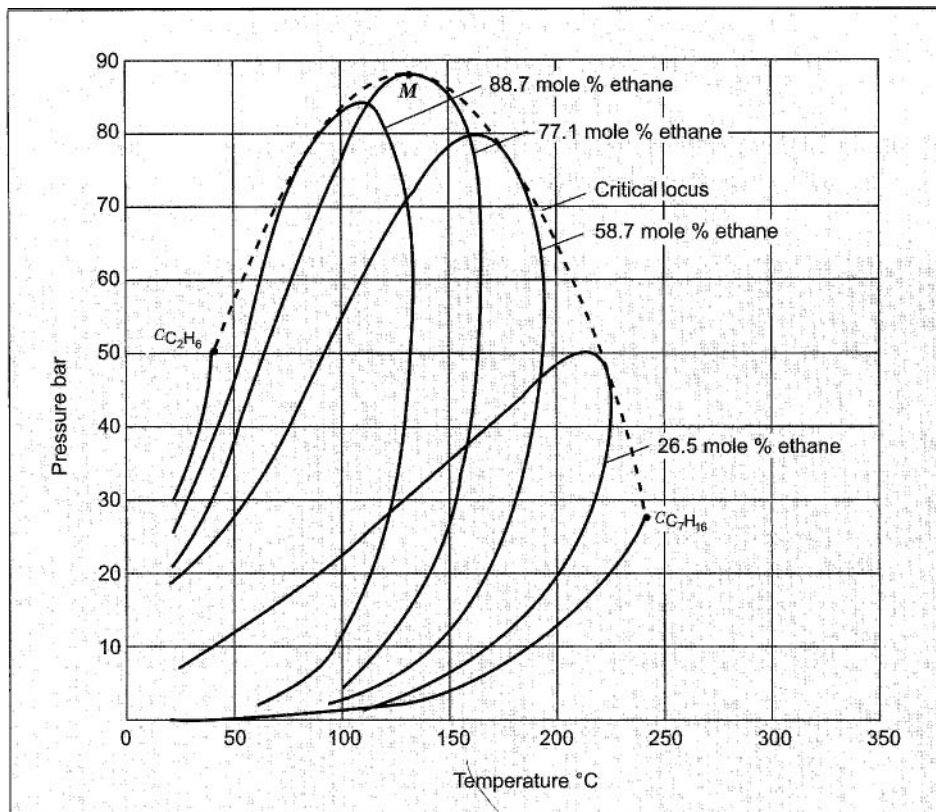[2]F. H. Ban-David, *AIChE J.*, vol. 2, p. 426, 1956.

Figure *10.5* PT diagram for ethaneln-heptane. (Redrawn from F. H. Barr-David, *AIChE* **J.**, vol. 2, pp. 426–427, 1956 with permission.)

The P-T diagram of Fig. 10.5 is typical for mixtures of nonpolar substances such as hydrocarbons. A P-T diagram for a very different kind of system, methanol(1)/benzene(2), is shown in Fig. 10.7. The nature of the curves in this figure suggests how difficult it can be to predict phase behavior for species so dissimilar as methanol and benzene.

Although VLE in the critical region is of considerable importance in the petroleum and natural-gas industries, most chemical processing is accomplished at much lower pressures. Figures 10.8 and 10.9 display common types of P-x-y and t-x-y behavior at conditions well removed from the critical region.

Figure 10.8(a) shows data for tetrahydrofuran(1)/carbon tetrachloride(2) at 303.15 K (30°C). Here, the P-x_1 or bubblepoint curve on a P-x_1-y_1 diagram lies below the linear P-x_1 relation characteristic of Raoult's-law behavior, as described in the following section. When such negative departures from linearity become sufficiently large relative to the difference between the two pure-species vapor pressures, the P-x curve exhibits a minimum, as illustrated in Fig. 10.8(b) for the chloroform(1)/tetrahydrofuran(2) system at 303.15 K (30°C). This figure shows that the P-y_1 curve also has a minimum at the same point. Thus at this point where $x_1 = y_1$ the dewpoint and bubblepoint curves are tangent to the same horizontal line. A boiling liquid of this composition produces a vapor of exactly the same composition, and
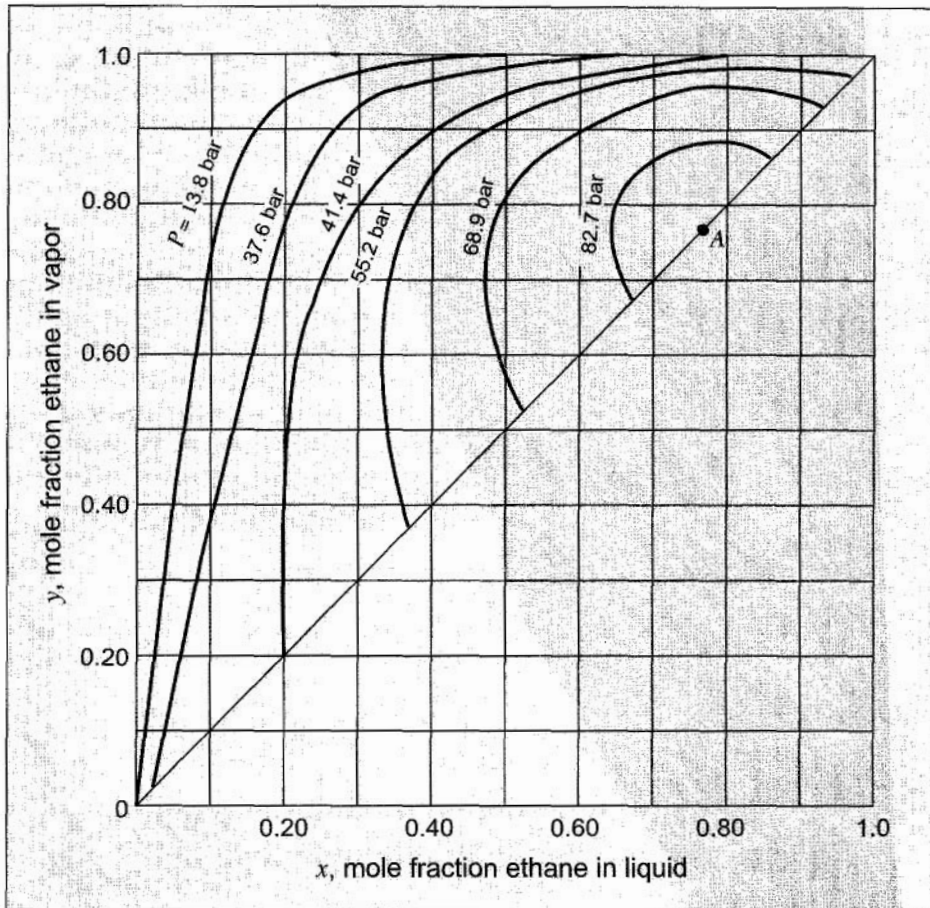
Figure *10.6   yx diagram for ethane/n-heptane. (Reproduced* **by** *permission from* F. H. *Barr-David, AIChE J., vol.* 2, p. 426–427, 1956.)

the liquid therefore does not change in composition as it evaporates. No separation of such a constant-boiling solution is possible by distillation. The term *azeotrope* is used to describe this state.[3]

The data for furan(1)/carbon tetrachloride(2) at 303.15 K (30°C) shown by Fig. 10.8(*c*) provide an example of a system for which the $P\text{-}x_1$ curve lies above the linear $P\text{-}x_1$ relation. The system shown in Fig. 10.8(*d*) for ethanol(1)/toluene(2) at 338.15 K (65°C) exhibits positive departures from linearity sufficiently large to cause a *maximum* in the $P\text{-}x_1$ curve. This state is a maximum-pressure azeotrope. Just as for the minimum-pressure azeotrope the vapor and liquid phases in equilibrium have the identical composition.

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[3]A compilation of data for such states is given by J. Gmehling, *Azeotropic Data,* John Wiley & Sons, Inc., New York, 1994.
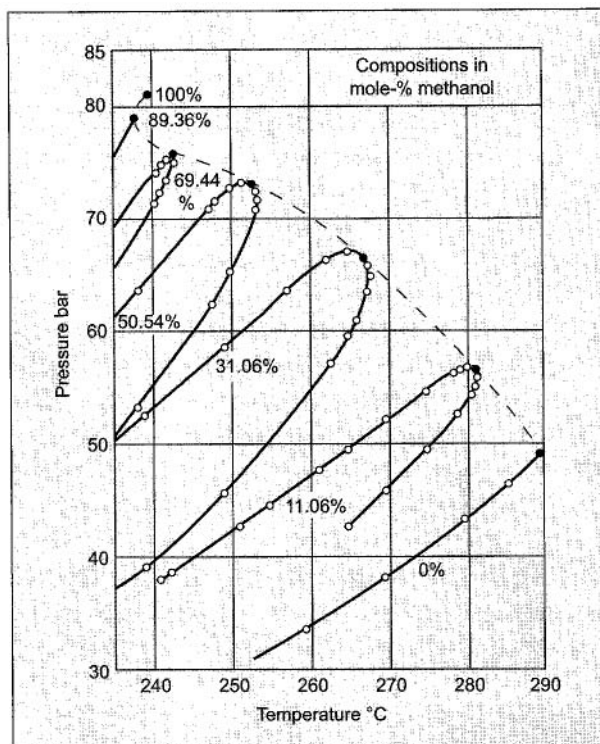
Figure 10.7 *PT* diagram for methanol/benzene. (Redrawn from *Chem. Eng. Sci.,* vol. 19, J. M. Skaates and W. B. Kay, "The phase relations of binary systems that form azeotropes," pp. 431–444, copyright 1964, with permission from Elsevier Science Ltd., Pergamon Imprint, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK)

Appreciable negative departures from P-x_1 linearity reflect stronger liquid-phase intermolecular attractions between unlike than between like pairs of molecules. Conversely, appreciable positive departures result for solutions for which liquid-phase intermolecular forces between like molecules are stronger than between unlike. In this latter case the forces between like molecules may be so strong as to prevent complete miscibility, and the system then forms two separate liquid phases over a range of compositions, as described in Sec. 14.4.

Since distillation processes are carried out more nearly at constant pressure than at constant temperature, t-x_1-y_1 diagrams of data at constant P are of practical interest. The four such diagrams corresponding to those of Fig. 10.8 are shown for atmospheric pressure in Fig. 10.9. Note that the dewpoint $(t$-$y_1)$ curves lie above the bubblepoint $(t$-$x_1)$ curves. Moreover, the minimum-pressure azeotrope of Fig. 10.8(b) appears as a maximum-temperature (or maximum-boiling) azeotrope on Fig. 10.9(b). There is an analogous correspondence between Figs. 10.8(d) and 10.9(d). The y_1-x_1 diagrams at constant P for the same four systems are shown in Fig. 10.10. The point at which a curve crosses the diagonal line of the diagram represents an azeotrope, for at such a point $y_1 = x_1$.
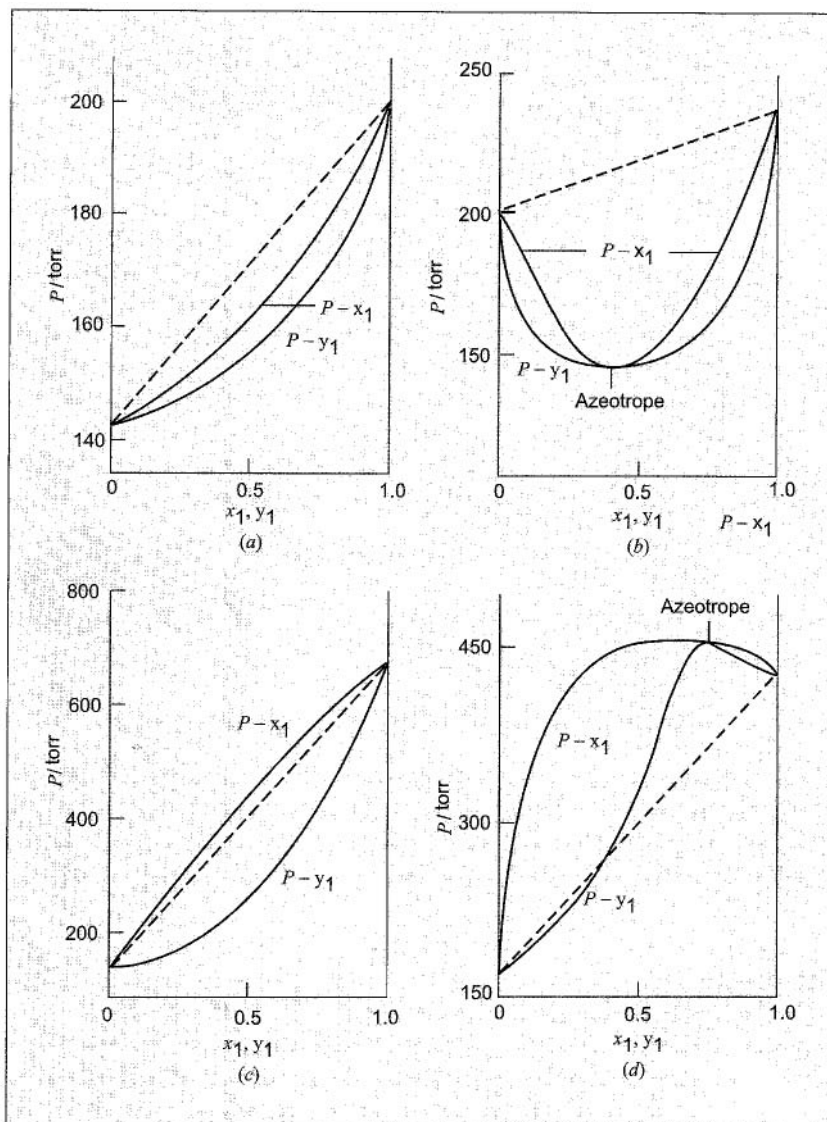
Figure 10.8 Pxy diagrams at constant T. (a) Tetrahydrofuran(1)/carbon tetrachloride(2) at 303.15 K (30°C); (b) chloroform(1)/tetrahydrofuran(2) at 303.15 K (30°C); (c) furan(1)/carbon tetrachloride(2) at 303.15 K (30°C); (d) ethanol(1)/toluene(2) at 338.15 K (65°C). Dashed lines: Px relation for ideal liquid solutions (Raoult's law)
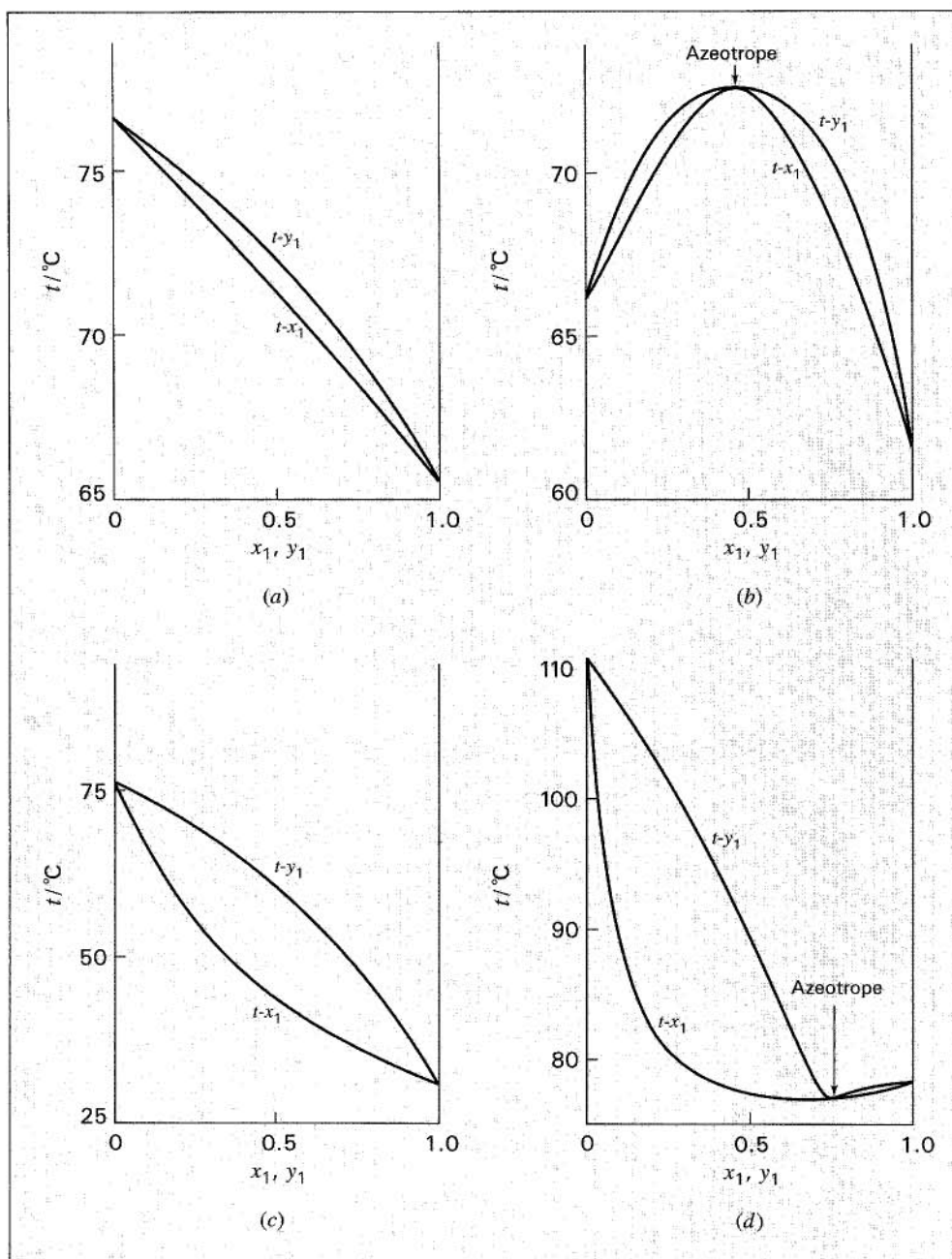
Figure 10.9 *txy* diagrams at 1 atm: (a) tetrahydrofuran(1)/carbon tetrachloride(2); *(b)*chloroform(1)/tetrahydrofuran(2); (c) furan(1)/carbon tetrachloride(2); *(d)*ethanol(1)/ toluene(2)
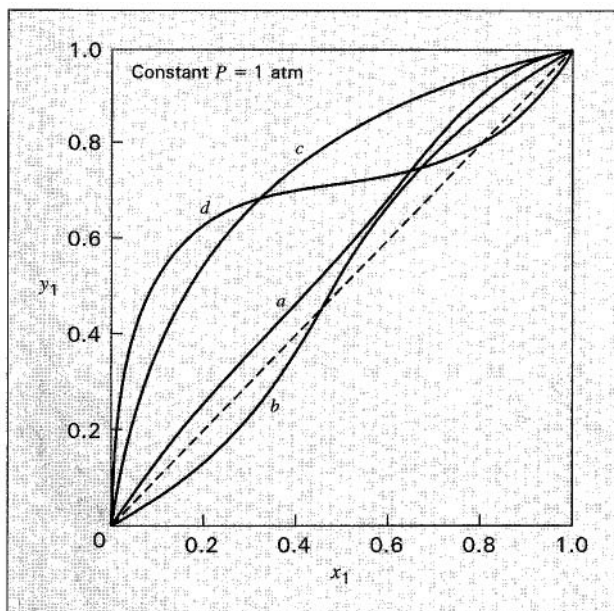
Figure 10.10 yx diagrams at 1 atm: (a) tetrahydrofuran(1)/carbon tetrachloride(2); (b) chloroform(1)/tetrahydrofuran(2); (c) furan(1)/carbon tetrachloride(2); *(d)*ethanol(1)/toluene(2)

10.4 SIMPLE MODELS FOR VAPOR/LIQUID EQUILIBRIUM

The preceding section has described what is observed through experimental observation. When thermodynamics is applied to vapor/liquid equilibrium, the goal is to find by calculation the temperatures, pressures, and compositions of phases in equilibrium. Indeed, thermodynamics provides the mathematical framework for the systematic correlation, extension, generalization, evaluation, and interpretation of data. Moreover, it is the means by which the predictions of various theories of molecular physics and statistical mechanics may be applied to practical purposes. None of this can be accomplished without *models* for the behavior of systems in vapor/liquid equilibrium. The two simplest are Raoult's law and Henry's law.

Raoult's Law

The two major assumptions required to reduce VLE calculations to *Raoult's law*[4] are:

- The vapor phase is an ideal gas.
- The liquid phase is an ideal solution (Sec. 11.8).

The first assumption means that Raoult's law can apply only for low to moderate pressures. The second implies that it can have approximate validity only when the species that comprise the system are chemically similar. Just as the ideal gas serves as a standard to which real-gas

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[4]Francois Marie Raoult (1830–1901), French chemist

behavior may be compared, the ideal solution represents a standard to which real-solution behavior may be compared. Ideal-solution behavior is often approximated by liquid phases wherein the molecular species are not too different in size and are of the same chemical nature. Thus, a mixture of isomers, such as *ortho*-, meta-, and para-xylene, conforms very closely to ideal-solution behavior. So do mixtures of adjacent members of a homologous series, as for example, n-hexaneln-heptane, ethanol/propanol, and benzene/toluene. Other examples are acetonelacetonitrile and acetonitrile/nitromethane.

The mathematical expression which reflects the two listed assumptions and which therefore gives quantitative expression to Raoult's law is:[5]

$$y_i P = x_i P_i^{\text{sat}} \qquad (i = 1, 2, \ldots, N) \tag{10.1}$$

where x_i is a liquid-phase mole fraction, y_i is a vapor-phase mole fraction, and P_i^{sat} is the vapor pressure of pure species i at the temperature of the system. The product $y_i P$ on the left side of Eq. (10.1) is known as the partial pressure of species i (Sec. 11.4).

The simple model for VLE represented by Eq. (10.1) provides a realistic description of actual behavior for a relatively small class of systems. Nevertheless, it is useful for displaying VLE calculations in their simplest form, and it also serves as a standard of comparison for more complex systems. A limitation of Raoult's law is that it can be applied only to species for which a vapor pressure is known, and this requires that the species be "subcritical," i.e., that the temperature of application be below the critical temperature of the species.

An important and useful feature of Raoult's law is that it is valid for any species present at a mole fraction approaching unity, provided only that the vapor phase is an ideal gas. Chemical similarity of the constituent species is not here a requirement.

Dewpoint and Bubblepoint Calculations with Raoult's Law

Although VLE problems with other combinations of variables are possible, engineering interest centers on dewpoint and bubblepoint calculations; there are four classes:

> BUBL P: Calculate $\{y_i\}$ and P, given $\{x_i\}$ and T
> DEW P: Calculate $\{x_i\}$ and P, given $\{y_i\}$ and T
> BUBL T: Calculate $\{y_i\}$ and T, given $\{x_i\}$ and P
> DEW T: Calculate $\{x_i\}$ and T, given $\{y_i\}$ and P

In each case the name suggests the quantities to be calculated: either a *BUBL* (vapor) or a DEW (liquid) composition and either P or T. Thus, one must specify either the liquid-phase or the vapor-phase composition and either T or P, thus fixing $1 + (N - 1)$ or N phase-rule variables, exactly the number of degrees of freedom F required by the phase rule [Eq. (2.7)] for vapor/liquid equilibrium. The equations for rigorous solution of VLE problems have a complex functionality, and their use to determine bubblepoints and dewpoints requires complicated iterative calculations (Secs. 14.1 and 14.2). In the following sections calculations are made for conditions where simplifying assumptions prevail. The general procedures for solution of VLE

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[5]The rigorous equation for subcritical vapor/liquid equilibrium, given by Eq. (14.1), reduces to Eq. (10.1) when the two listed assumptions are imposed.

problems thus become evident through calculations of relative simplicity. We focus first on the application of Raoult's law.

Because $\sum_i y_i = 1$, Eq. (10.1) may be summed over all species to yield:

$$P = \sum_i x_i P_i^{\text{sat}} \tag{10.2}$$

This equation finds application in bubblepoint calculations, where the vapor-phase composition is unknown. For a binary system with $x_2 = 1 - x_1$,

$$P = P_2^{\text{sat}} + (P_1^{\text{sat}} - P_2^{\text{sat}})x_1$$

and a plot of P vs. x_1 at constant temperature is a straight line connecting P_2^{sat} at $x_1 = 0$ with P_1^{sat} at $x_1 = 1$. The P-x-y diagrams of Fig. 10.8 show this linear relation.

Equation (10.1) may also be solved for x_i and summed over all species. With $\sum_i x_i = 1$, this yields:

$$P = \frac{1}{\sum_i y_i / P_i^{\text{sat}}} \tag{10.3}$$

an equation applied in dewpoint calculations, where liquid-phase compositions are not known.

Example 10.1

Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{\text{sat}}/\text{kPa} = 14.2724 - \frac{2945.47}{T - 49.15}$$

$$\ln P_2^{\text{sat}}/\text{kPa} = 14.2043 - \frac{2972.64}{T - 64.15}$$

(a) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 348.15 K (75°C).

(b) Prepare a graph showing t vs. x_1 and t vs. y_1 for a pressure of 70 kPa.

Solution 10.1

(a) *BUBL P* calculations are required. The basis is the binary-system form of Eq. (10.2), repeated here as:

$$P = P_2^{\text{sat}} + (P_1^{\text{sat}} - P_2^{\text{sat}})x_1 \tag{A}$$

At 348.15 K (75°C), by the Antoine equations,

$$P_1^{\text{sat}} = 83.21 \quad \text{and} \quad P_2^{\text{sat}} = 41.98 \text{ kPa}$$

Calculations are here very simple, as illustrated for $x_1 = 0.6$:

$$P = 41.98 + (83.21 - 41.98)(0.6) = 66.72 \text{ kPa}$$

The corresponding value of y_1 is then found from Eq. (10.1):

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483$$

These results mean that at 348.15 K (75°C) a liquid mixture of 60 mol-% acetonitrile and 40 mol-% nitromethane is in equilibrium with a vapor containing 74.83 mol-% acetonitrile at a pressure of 66.72 kPa. The results of calculations for 348.15 K (75°C) at a number of values of x_1 are tabulated as follows:

x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0	0.0000	41.98	0.6	0.7483	66.72
0.2	0.3313	50.23	0.8	0.8880	74.96
0.4	0.5692	58.47	1.0	1.0000	83.21

These same results are shown by the P-x_1-y_1 diagram of Fig. 10.11. This figure is a phase diagram on which the straight line labeled P-x_1 represents states of saturated liquid; the subcooled-liquid region lies above this line. The curve labeled P-y_1 represents states of saturated vapor; the superheated-vapor region lies below this curve. Points lying between the saturated-liquid and saturated-vapor lines are in the two-phase region, where saturated liquid and saturated vapor coexist in equilibrium. The P-x_1 and P-y_1 lines meet at the edges of the diagram, where saturated liquid and saturated vapor of the pure species coexist at the vapor pressures P_1^{sat} and P_2^{sat}.

To illustrate the nature of phase behavior in this binary system we follow the course of a constant-temperature process on the P-x_1-y_1 diagram. Imagine a sub-cooled liquid mixture of 60 mol-% acetonitrile and 40 mol-% nitromethane existing in a piston/cylinder arrangement at 348.15 K (75°C). Its state is represented by point a in Fig. 10.11. Withdrawing the piston slowly enough reduces the pressure while maintaining the system at equilibrium at 348.15 K (75°C). Since the system is closed, the overall composition remains constant during the process, and the states of the system *as a whole* fall on the vertical line descending from point a. When the pressure reaches the value at point b, the system is saturated liquid on the verge of vaporizing. A minuscule further decrease in pressure produces a bubble of vapor, represented by point b'. The two points b and b' ($x_1 = 0.6$, $P = 66.72$ kPa, and $y_1 = 0.7483$) together represent the state determined by earlier calculations. Point b is a bubblepoint, and the P-x_1 line is the locus of bubblepoints.

As the pressure is further reduced, the amount of vapor increases and the amount of liquid decreases, with the states of the two phases following paths $b'c$ and bc', respectively. The dotted line from point b to point c represents the *overall* states of the two-phase system. Finally, as point c is approached, the liquid phase, represented by point c', has almost disappeared, with only droplets (dew) remaining. Point c is therefore a dewpoint, and the P-y_1 curve is the locus of dewpoints. Once the dew has evaporated, only saturated vapor at point c remains, and further pressure reduction leads to superheated vapor at point d.
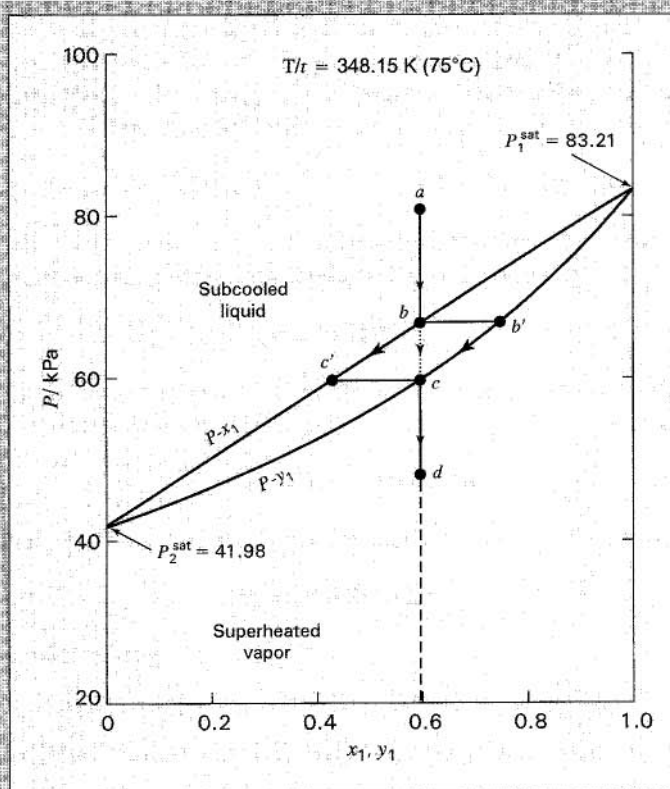
Figure 10.11 Pxy diagram for acetonitrile(1)/nitromethane(2) at 348.15 K (75°C) as given by Raoult's law

The composition of the vapor at point c is $y_1 = 0.6$, but the composition of the liquid at point c' and the pressure must either be read from the graph or calculated. This is a *DEW P* calculation, and by Eq. (10.3),

$$P = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat}}$$

For $y_1 = 0.6$ and $T/t = 348.15$ K (75°C),

$$P = \frac{1}{0.6/83.21 + 0.4/41.98} = 59.74 \text{ kPa}$$

By Eq. (10.1),

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{(0.6)(59.74)}{83.21} = 0.4308$$

This is the liquid-phase composition at point c'.

(b) When pressure P is fixed, the temperature varies along with x_1 and y_1. For a given pressure, the temperature range is bounded by the saturation temperatures

T_1^{sat} and T_2^{sat}, the temperatures at which the pure species exert vapor pressures equal to P. For the present system, these temperatures are calculated from the Antoine equations:

$$T_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i$$

For $P = 70$ kPa, $T_1^{sat}/t_1^{sat} = 342.99$ K/69.84°C and $T_2^{sat}/t_2^{sat} = 362.73$ K/89.58°C. The simplest way to prepare a T-x_1-y_1 diagram is to select values of T between these two temperatures, calculate P_1^{sat} and P_2^{sat} for these temperatures, and evaluate x_1 by Eq. (A), written:

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

For example, at 351.15 K (78°C), $P_1^{sat} = 91.76$ kPa, $P_2^{sat} = 46.84$ kPa, and

$$x_1 = \frac{70 - 46.84}{91.76 - 46.84} = 0.5156$$

By Eq. (10.1),

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.5156)(91.76)}{70} = 0.6759$$

The results of this and similar calculations for $P = 70$ kPa are as follows:

x_1	y_1	T/t(K/°C)	x_1	y_1	T/t(K/°C)
0.0000	0.0000	362.73 (89.58) $T_2^{sat}/(t_2^{sat})$	0.5156	0.6759	351.15 (78)
0.1424	0.2401	359.15 (86)	0.7378	0.8484	347.15 (74)
0.3184	0.4742	355.15 (82)	1.0000	1.0000	342.99 (69.84) $T_1^{sat}/(t_1^{sat})$

Figure 10.12 is the t-x_1-y_1 diagram showing these results. On this phase diagram, drawn for a constant pressure of 70 kPa, the t-y_1 curve represents states of saturated vapor, with states of superheated vapor lying above it. The t-x_1 curve represents states of saturated liquid, with states of subcooled liquid lying below it. The two-phase region lies between these curves.

With reference to Fig. 10.12, consider a constant-pressure heating process leading from a state of subcooled liquid at point a to a state of superheated vapor at point d. The path shown on the figure is for a constant overall composition of 60 mol-% acetonitrile. The temperature of the liquid increases as the result of heating from point a to point b, where the first bubble of vapor appears. Thus point b is a bubblepoint, and the t-x_1 curve is the locus of bubblepoints.

For $x_1 = 0.6$ and $P = 70$ kPa, T/t is determined by a *BUBL T* calculation, which requires iteration. Equation (10.2) is here written:
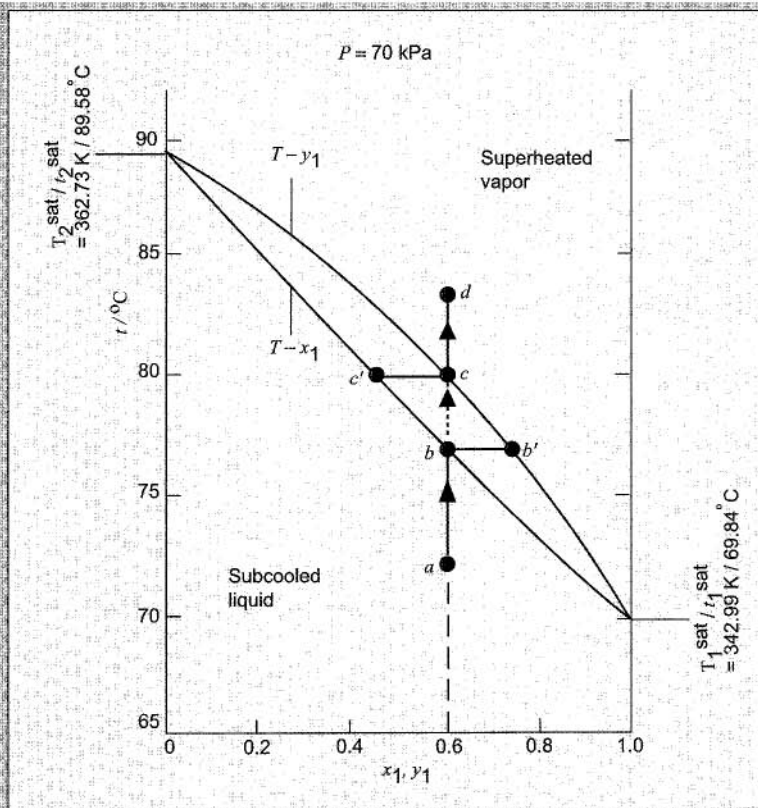
$$P_2^{sat} = \frac{P}{x_1 \alpha + x_2} \qquad (B)$$

Figure 10.12 txy diagram for acetonitrile(1)/nitromethane(2) at 70 kPa as given by Raoult's law

where $\alpha = P_1^{sat}/P_2^{sat}$. Subtracting $\ln P_2^{sat}$ from $\ln P_1^{sat}$ as given by the Antoine equations yields:

$$\ln \alpha = 0.0681 - \frac{2945.47}{T - 49.15} + \frac{2972.64}{T - 64.15} \qquad (C)$$

The reason for introducing α is that as the controlling variable it is far less sensitive to t than an individual vapor pressure. An initial value of α is found for an arbitrary intermediate temperature. Iteration is then as follows:

- With the current value of α, calculate P_2^{sat} by Eq. (B).
- Calculate T from the Antoine equation for species 2:

$$T = \frac{2972.64}{14.2043 - \ln P_2^{sat}} + 64.15$$

- Find a new value of α by Eq. (C).
- Return to the initial step and iterate to convergence for a final value of T.

The result is $T/t = 349.57$ K$/76.42°$C, the temperature of points b and b'. From the Antoine equation, $P_1^{\text{sat}} = 87.17$ kPa, and by Eq. (10.1) the composition at point b' is:

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = \frac{(0.6)(87.17)}{70} = 0.7472$$

Vaporizing a mixture at constant pressure, unlike vaporizing a pure species, does not in general occur at constant temperature. As the heating process continues beyond point b, the temperature rises, the amount of vapor increases, and the amount of liquid decreases. During this process, the vapor- and liquid-phase compositions change as indicated by paths $b'c$ and bc', until the dewpoint is reached at point c, where the last droplets of liquid disappear. The t-y_1 curve is the locus of dewpoints.

The vapor composition at point c is $y = 0.6$; because the pressure is also known ($P = 70$ kPa), a *DEW T* calculation is possible. With $\alpha = P_1^{\text{sat}}/P_2^{\text{sat}}$, Eq. (10.3) is written:

$$P_1^{\text{sat}} = P(y_1 + y_2\alpha)$$

The iteration steps are as before, but are based on P_1^{sat} rather than P_2^{sat}, with

$$T = \frac{2945.47}{14.2724 - \ln P_1^{\text{sat}}} + 49.15$$

The result here is $T/t = 352.73$ K $/79.58°$C, the temperature of points c and c'. From the Antoine equation, $P_1^{\text{sat}} = 96.53$ kPa, and Eq. (10.1) gives the composition at point c':

$$x_1 = \frac{y_1 P}{P_1^{\text{sat}}} = \frac{(0.6)(70)}{96.53} = 0.4351$$

Thus the temperature rises from 349.57 to 352.73 K (76.42 to 79.58°C) during the vaporization step from point b to point c. Continued heating simply superheats the vapor to point d.

Henry's Law

Application of Raoult's law to species i requires a value for P_i^{sat} at the temperature of application, and thus is not appropriate for a species whose critical temperature is less than the temperature of application. If a system of air in contact with liquid water is presumed at equilibrium, then the air is saturated with water. The mole fraction of water vapor in the air is usually found from Raoult's law applied to the water with the assumption that no air dissolves in the liquid phase. Thus, the liquid water is regarded as pure and Raoult's law for the water (species 2) becomes $y_2 P = P_2^{\text{sat}}$. At 298.15 K (25°C) and atmospheric pressure, this equation yields:

$$y_2 = \frac{P_2^{\text{sat}}}{P} = \frac{3.166}{101.33} = 0.0312$$

where the pressures are in kPa, and P_2^{sat} comes from the steam tables.

Table 10.1   Henry's Constants for Gases Dissolved
in Water at 298.15 K (25°C)

Gas	$\mathcal{H}$/bar	Gas	$\mathcal{H}$/bar
Acetylene	1 350	Helium	126 600
Air	72 950	Hydrogen	71 600
Carbon dioxide	1 670	Hydrogen sulfide	55 200
Carbon monoxide	54 600	Methane	41 850
Ethane	30 600	Nitrogen	87 650
Ethylene	11 550	Oxygen	44 380

If one wishes to calculate the mole fraction of air dissolved in the water, then Raoult's
law cannot be applied, because the critical temperature of air is much lower than 298.15 K
(25°C). This problem can be solved by Henry's law, applied here for pressures low enough
that the vapor phase may be assumed an ideal gas. For a species present as a very dilute solute
in the liquid phase, Henry's law then states that the partial pressure of the species in the vapor
phase is directly proportional to its liquid-phase mole fraction. Thus,

$$\boxed{y_i P = x_i \mathcal{H}_i}$$ (10.4)

where $\mathcal{H}_i$ is *Henry's constant*. Values of $\mathcal{H}_i$ come from experiment, and Table 10.1 lists
values at 298.15 K (25°C) for a few gases dissolved in water. For the air/water system at
298.15 K (25°C) and atmospheric pressure, Henry's law applied to the air (species 1) with
$y_1 = 1 - 0.0312 = 0.9688$ yields:

$$x_1 = \frac{y_1 P}{\mathcal{H}_1} = \frac{(0.9688)(101.33)}{72\ 950} = 1.35 \times 10^{-5}$$

This result justifies the assumption made in application of Raoult's law to the water.

Example 10.2

Assuming that carbonated water contains only CO_2 and H_2O, determine the composi-
tions of the vapor and liquid phases in a sealed can of "soda" and the pressure exerted
on the can at 283.15 K (10°C). Henry's constant for CO_2 in water at 283.15 K (10°C)
is about 990 bar.

Solution 10.2

Take species 1 as the CO_2 and species 2 as the water. Henry's law for species 1
and Raoult's law for species 2 are written:

$$y_1 P = x_1 \mathcal{H}_1 \qquad\qquad y_2 P = x_2 P_2^{sat}$$

These equations are added to give:

$$P = x_1 \mathcal{H}_1 + x_2 P_2^{sat}$$

Assume for the moment that the mole fraction of CO_2 in the liquid is $x_1 = 0.01$. With $\mathcal{H}_1 = 990$ bar and $P_2^{sat} = 0.012\ 27$ bar [from the steam tables at 283.15 K (10°C)],

$$P = (0.01)(990) + (0.99)(0.012\ 27) = 9.912 \text{ bar}$$

This result is used in Henry's law to determine a new value for x_1. With $y_1 \approx 1$, Eq. (10.4) written for species 1 becomes:

$$x_1 = \frac{P}{\mathcal{H}_1} = \frac{9.912}{990} = 0.0100$$

which confirms the original assumption. Then by Raoult's law, Eq. (10.1) written for species 2,

$$y_2 = \frac{x_2 P_2^{sat}}{P} = \frac{(0.99)(0.012\ 27)}{9.912} = 0.0012$$

Whence $y_1 = 1 - y_2 = 1 - 0.0012 = 0.9988$, and the vapor phase is nearly pure CO_2, as assumed.

10.5 VLE BY MODIFIED RAOULT'S LAW

For low to moderate pressures a much more realistic equation for VLE results when the second major Raoult's-law assumption is abandoned, and account is taken of deviations from solution ideality in the liquid phase by a factor inserted into Raoult's law, modified to read:

$$\boxed{y_i P = x_i \gamma_i P_i^{sat} \qquad (i = 1, 2, \ldots, N)} \qquad (10.5)$$

The factor γ_i is called an *activity coefficient*. Bubblepoint and dewpoint calculations made with this equation are only a bit more complex than the same calculations made with Raoult's law. Activity coefficients are functions of temperature and liquid-phase composition, and ultimately are based on experiment (Sec. 12.1). For present purposes, the necessary values are assumed known.[6]

Because $\sum_i y_i = 1$, Eq. (10.5) may be summed over all species to yield:

$$P = \sum x_i \gamma_i P_i^{sat} \qquad (10.6)$$

Alternatively, Eq. (10.5) may be solved for *xi,* in which case summing over all species yields:

$$P = \frac{1}{\sum y_i / \gamma_i P_i^{sat}} \qquad (10.7)$$

[6]The correlation of activity-coefficient data is treated in Secs. 12.1 and 12.2.

Example 10.3

For the system methanol(1)/methyl acetate(2), the following equations provide a reasonable correlation for the activity coefficients:

$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2 \qquad \text{where} \qquad A = 2.771 - 0.005\,23T$$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{\text{sat}} = 16.591\,58 - \frac{3643.31}{T - 33.424} \qquad \ln P_2^{\text{sat}} = 14.253\,26 - \frac{2665.54}{T - 53.424}$$

where T is in kelvins and the vapor pressures are in kPa. Assuming the validity of Eq. (10.5), calculate:

(a) P and $\{y_i\}$, for $T = 318.15$ K (45°C) and $x_1 = 0.25$.
(b) P and $\{x_i\}$, for $T = 318.15$ K (45°C) and $y_1 = 0.60$.
(c) T and $\{y_i\}$, for $P = 101.33$ kPa and $x_1 = 0.85$.
(d) T and $\{x_i\}$, for $P = 101.33$ kPa and $y_1 = 0.40$.
(e) The azeotropic pressure, and the azeotropic composition, for $T = 318.15$ K (45°C).

Solution 10.3

(a) A *BUBL P* calculation. For $T = 318.15$ K, the Antoine equations yield:

$$P_1^{\text{sat}} = 44.51 \qquad \text{and} \qquad P_2^{\text{sat}} = 65.64 \text{ kPa}$$

Activity coefficients are calculated from the correlating equations:

$$A = 2.771 - (0.005\,23)(318.15) = 1.107$$

$$\gamma_1 = \exp(A x_2^2) = \exp\left[(1.107)(0.75)^2\right] = 1.864$$

$$\gamma_2 = \exp(A x_1^2) = \exp\left[(1.107)(0.25)^2\right] = 1.072$$

The pressure is given by Eq. (10.6):

$$P = (0.25)(1.864)(44.51) + (0.75)(1.072)(65.64) = 73.50 \text{ kPa}$$

By Eq. (10.5) written, $y_i = x_i \gamma_i P_i^{\text{sat}}/P$,

$$y_1 = 0.282 \qquad \text{and} \qquad y_2 = 0.718$$

(b) A *DEW P* calculation. With T unchanged from part (a), the values of P_1^{sat}, P_2^{sat}, and A are unchanged. However, the liquid-phase composition is here unknown, but is required in the calculation of activity coefficients. An iterative procedure is therefore indicated, and for initial values we set $\gamma_1 = \gamma_2 = 1.0$. The required steps, carried out with current values of γ_1 and γ_2, are:

- Calculate P by Eq. (10.7), written:

$$P = \frac{1}{y_1/\gamma_1 P_1^{\text{sat}} + y_2/\gamma_2 P_2^{\text{sat}}}$$

- Calculate x_1 by Eq. (10.5):

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{\text{sat}}} \qquad \text{then} \qquad x_2 = 1 - x_1$$

- Evaluate activity coefficients; go to first step; continue to convergence.

When carried through, this process leads to the final values:

$$P = 62.89 \text{ kPa} \qquad x_1 = 0.8169 \qquad \gamma_1 = 1.0378 \qquad \gamma_2 = 2.0935$$

(c) A *BUBL T* calculation. An initial value for the unknown temperature is found from the saturation temperatures of the pure species at the known pressure. The Antoine equation, solved for T, becomes:

$$T_i^{\text{sat}} = \frac{B_i}{A_i - \ln P} - C_i$$

Application for $P = 101.33$ kPa leads to:

$$T_1^{\text{sat}} = 337.71 \text{ K} \qquad \text{and} \qquad T_2^{\text{sat}} = 330.08 \text{ K}$$

A mole-fraction-weighted average of these values then provides an initial T:

$$T = (0.85)(337.71) + (0.15)(330.08) = 336.57 \text{ K}$$

An iterative procedure consists of the steps:

- For the current value of T calculate values for A, γ_1, γ_2, and $\alpha \equiv P_1^{\text{sat}}/P_2^{\text{sat}}$ from the given equations.
- Find a new value for P_1^{sat} from Eq. (10.6) written:

$$P_1^{\text{sat}} = \frac{P}{x_1\gamma_1 + x_2\gamma_2/\alpha}$$

- Find a new value for T from the Antoine equation written for species 1:

$$T = \frac{B_1}{A_1 - \ln P_1^{\text{sat}}} - C_1$$

- Return to the initial step; iterate to convergence on a value for T.

This process yields the final values:

$$T = 331.20 \text{ K } (58.05\,^{\circ}\text{C}) \qquad P_1^{\text{sat}} = 95.24 \text{ kPa} \qquad P_2^{\text{sat}} = 48.73 \text{ kPa}$$

$$A = 1.0388 \qquad \gamma_1 = 1.0236 \qquad \gamma_2 = 2.1182$$

The vapor-phase mole fractions are given by:

$$y_1 = \frac{x_1\gamma_1 P_1^{\text{sat}}}{P} = 0.670 \qquad \text{and} \qquad y_2 = 1 - y_1 = 0.330$$

(d) A *DEW T* calculation. Since $P = 101.33$ kPa, the saturation temperatures are the same as those of part (c), and an initial value for the unknown temperature is

found as a mole-fraction weighted average of these values:

$$T = (0.40)(337.71) + (0.60)(330.08) = 333.13 \text{ K}$$

Since the liquid-phase composition is not known, the activity coefficients are initialized as $\gamma_1 = \gamma_2 = 1$. As in part (c) an iterative procedure is indicated:

- Evaluate A, P_1^{sat}, P_2^{sat}, and $\alpha \equiv P_1^{sat}/P_2^{sat}$ at the current value of T from the Antoine equations.
- Calculate x_1 by Eq. (10.5):

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} \qquad \text{then} \qquad x_2 = 1 - x_1$$

- Calculate values of γ_1 and γ_2 from the correlating equations.
- Find a new value for P_1^{sat} from Eq. (10.7) written:

$$P_1^{sat} = P\left(\frac{y_1}{\gamma_1} + \frac{y_2}{\gamma_2}\alpha\right)$$

- Find a new value for T from the Antoine equation written for species 1:

$$T = \frac{B_1}{A_1 - \ln P_1^{sat}} - C_1$$

- Return to the initial step and iterate with the current values of γ_1 and γ_2 until the process converges on a final value of T.

The process yields the final values:

$$T = 326.70 \text{ K} (53.55 \text{ C}) \qquad P_1^{sat} = 64.63 \text{ kPa} \qquad P_2^{sat} = 90.89 \text{ kPa}$$
$$A = 1.0624 \qquad \gamma_1 = 1.3629 \qquad \gamma_2 = 1.2523$$
$$x_1 = 0.4602 \qquad x_2 = 0.5398$$

(e) First determine whether or not an azeotrope exists at the given temperature. This calculation is facilitated by the definition of a quantity called the *relative volatility*:

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \tag{10.8}$$

At an azeotrope $y_1 = x_1$, $y_2 = x_2$, and $\alpha_{12} = 1$. In general, by Eq. (10.5),

$$\frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P}$$

Therefore,

$$\alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}} \tag{10.9}$$

The correlating equations for the activity coefficients show that when $x_1 = 0$, $\gamma_2 = 1$, and $\gamma_1 = \exp(A)$; when $x_1 = 1$, $\gamma_1 = 1$ and $\gamma_2 = \exp(A)$. Therefore in these limits,

$$(\alpha_{12})_{x_1=0} = \frac{P_1^{sat}\exp(A)}{P_2^{sat}} \qquad \text{and} \qquad (\alpha_{12})_{x_1=1} = \frac{P_1^{sat}}{P_2^{sat}\exp(A)}$$

Values of P_1^{sat}, P_2^{sat}, and A are given in part (a) for the temperature of interest. The limiting values of α_{12} are therefore:

$$(\alpha_{12})_{x_1=0} = \frac{(44.51)\exp(1.107)}{65.64} = 2.052$$

$$(\alpha_{12})_{x_1=1} = \frac{44.51}{(65.64)\exp(1.107)} = 0.224$$

Since the value at one limit is greater than 1, whereas the value at the other limit is less than 1, an azeotrope does exist, because α_{12} is a continuous function of x_1 and must pass through the value of 1.0 at some intermediate composition.

For the azeotrope, $\alpha_{12} = 1$, and Eq. (10.9) becomes:

$$\frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{sat}}{P_1^{sat}} = \frac{65.64}{44.51} = 1.4747$$

The difference between the correlating equations for $\ln\gamma_1$ and $\ln\gamma_2$ provides the general relation:

$$\ln\frac{\gamma_1}{\gamma_2} = Ax_2^2 - Ax_1^2 = A(x_2 - x_1)(x_2 + x_1) = A(x_2 - x_1) = A(1 - 2x_1)$$

Thus the azeotropic composition is the value of x_1 for which this equation is satisfied when the activity-coefficient ratio has its azeotrope value of 1.4747; i.e., for which:

$$\ln\frac{\gamma_1}{\gamma_2} = \ln 1.4747 = 0.388$$

Solution gives $x_1^{az} = 0.325$. For this value of x_1, $\gamma_1^{az} = 1.657$. With $x_1^{az} = y_1^{az}$, Eq. (10.5) becomes:

$$P^{az} = \gamma_1^{az} P_1^{sat} = (1.657)(44.51)$$

Thus, $P^{az} = 73.76$ kPa $x_1^{az} = y_1^{az} = 0.325$

Dewpoint and bubblepoint calculations are readily made with software packages such as Mathcad® and Maple®, in which iteration is an integral part of an equation-solving routine. Mathcad programs for solution of Ex. 10.3, parts (a) through (d), are given in App. D.2.

Calculations for multicomponent systems made without simplifying assumptions are readily carried out in like manner by computer. The procedures are presented in Sec. 14.1.

10.6 VLE FROM K-VALUE CORRELATIONS

A convenient measure of the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases is the equilibrium ratio K_i, defined as:

$$K_i \equiv \frac{y_i}{x_i} \qquad (10.10)$$

This quantity is usually called simply a *K-value*. Although it adds nothing to thermodynamic knowledge of VLE, it does serve as a measure of the "lightness" of a constituent species, i.e., of

its tendency to favor the vapor phase. When K_i is greater than unity, species **i** exhibits a higher concentration in the vapor phase; when less, a higher concentration in the liquid phase, and is considered a "heavy" constituent. Moreover, the use of K-values makes for computational convenience, allowing elimination of one set of mole fractions $\{y_i\}$ or $\{xi)$ in favor of the other.

Reference to Eq. (10.1) shows that the K-value for Raoult's law is:

$$K_i = \frac{P_i^{\text{sat}}}{P} \tag{10.11}$$

and reference to Eq. (10.5) shows that for modified Raoult's law it is:

$$K_i = \frac{\gamma_i P_i^{\text{sat}}}{P} \tag{10.12}$$

According to Eq. (10.10), $y_i = K_i x_i$; because $\sum_i y_i = 1$, then

$$\sum_i K_i x_i = 1 \tag{10.13}$$

Thus for bubblepoint calculations, where the x_i are known, the problem is to find the set of K-values that satisfies Eq. (10.13). Alternatively, Eq. (10.10) can be written, $x_i = y_i/K_i$; because $\sum_i x_i = 1$, then

$$\sum_i \frac{y_i}{K_i} = 1 \tag{10.14}$$

Thus for dewpoint calculations, where the y_i are known, the problem is to find the set of K-values that satisfies Eq. (10.14).

Equations (10.11) and (10.12) together with Eq. (10.10) represent alternative forms of Raoult's law and modified Raoult's law. The great attraction of Raoult's law is that it expresses K-values as functions of just T and P, independent of the compositions of the liquid and vapor phases. Where the assumptions which underlie Raoult's law are appropriate, this allows K-values to be calculated and correlated as functions of T and P. For mixtures of light hydrocarbons and other simple molecules, in which the molecular force fields are relatively uncomplicated, correlations of this kind have approximate validity. Figures 10.13 and 10.14, show nomographs for the K-values of light hydrocarbons as functions of T and P, prepared by Dadyburjor.[7] They do allow for an *average* effect of composition, but the essential basis is Raoult's law.

Example 10.4

For a mixture of 10 mol-% methane, 20 mol-% ethane, and 70 mol-% propane at 283.15 K (10 °C), determine:

(a) The dewpoint pressure.
(b) The bubblepoint pressure.

The K-values are given by Fig. 10.13.

[7]D. B. Dadyburjor, *Chem. Eng. Progr.*, vol. 74(4), pp. 85–86, April, 1978
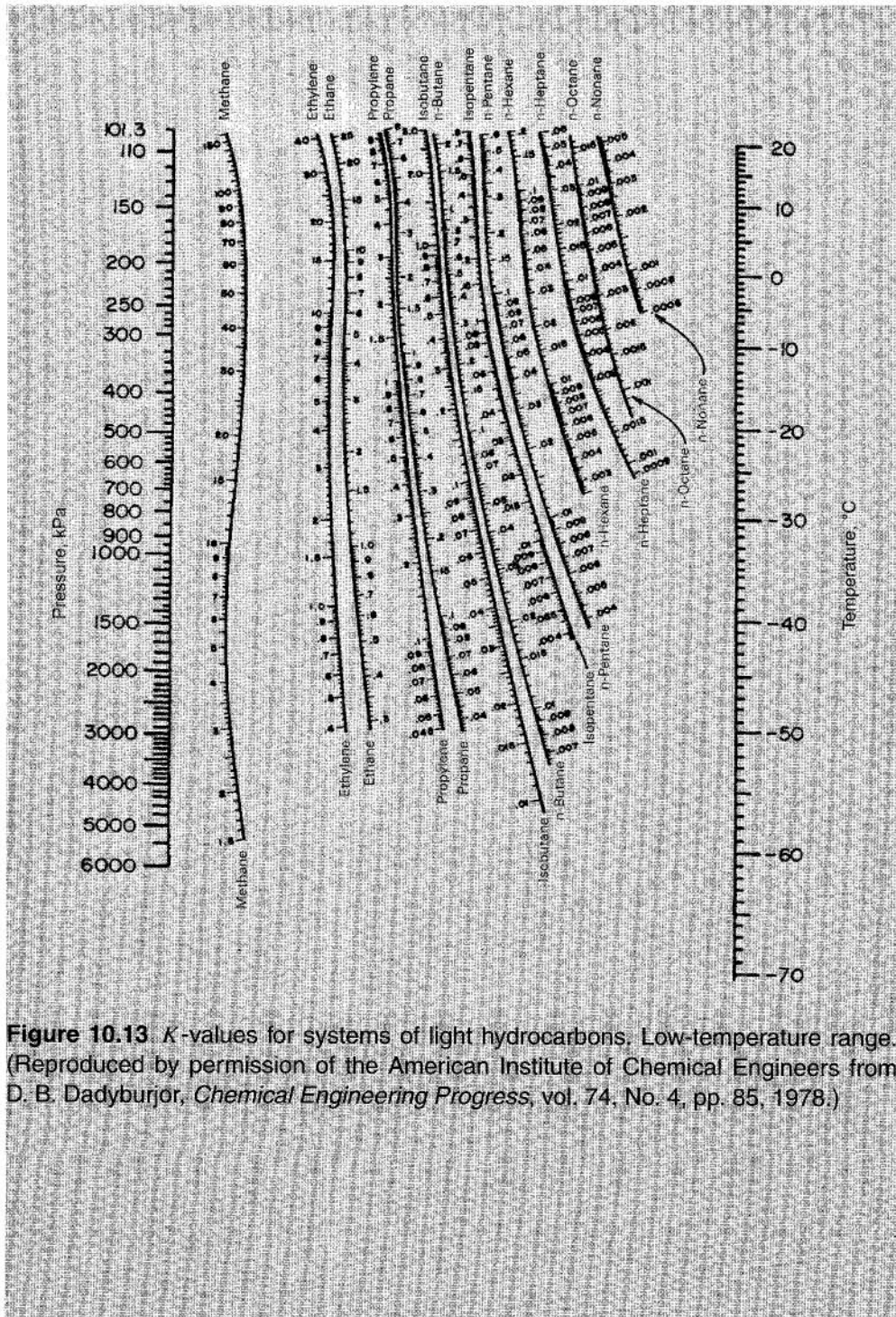
Figure 10.13 *K*-values for systems of light hydrocarbons. Low-temperature range. (Reproduced by permission of the American Institute of Chemical Engineers from D. B. Dadyburjor, *Chemical Engineering Progress*, vol. 74, No. 4, pp. 85, 1978.)

Figure 10.14 K-values for systems of light hydrocarbons. High-temperature range. (Reproduced by permission of the American Institute of Chemical Engineers from D. B. Dadyburjor, *Chemical Engineering Progress*, vol. 74, No. 4, pp. 86, 1978.)
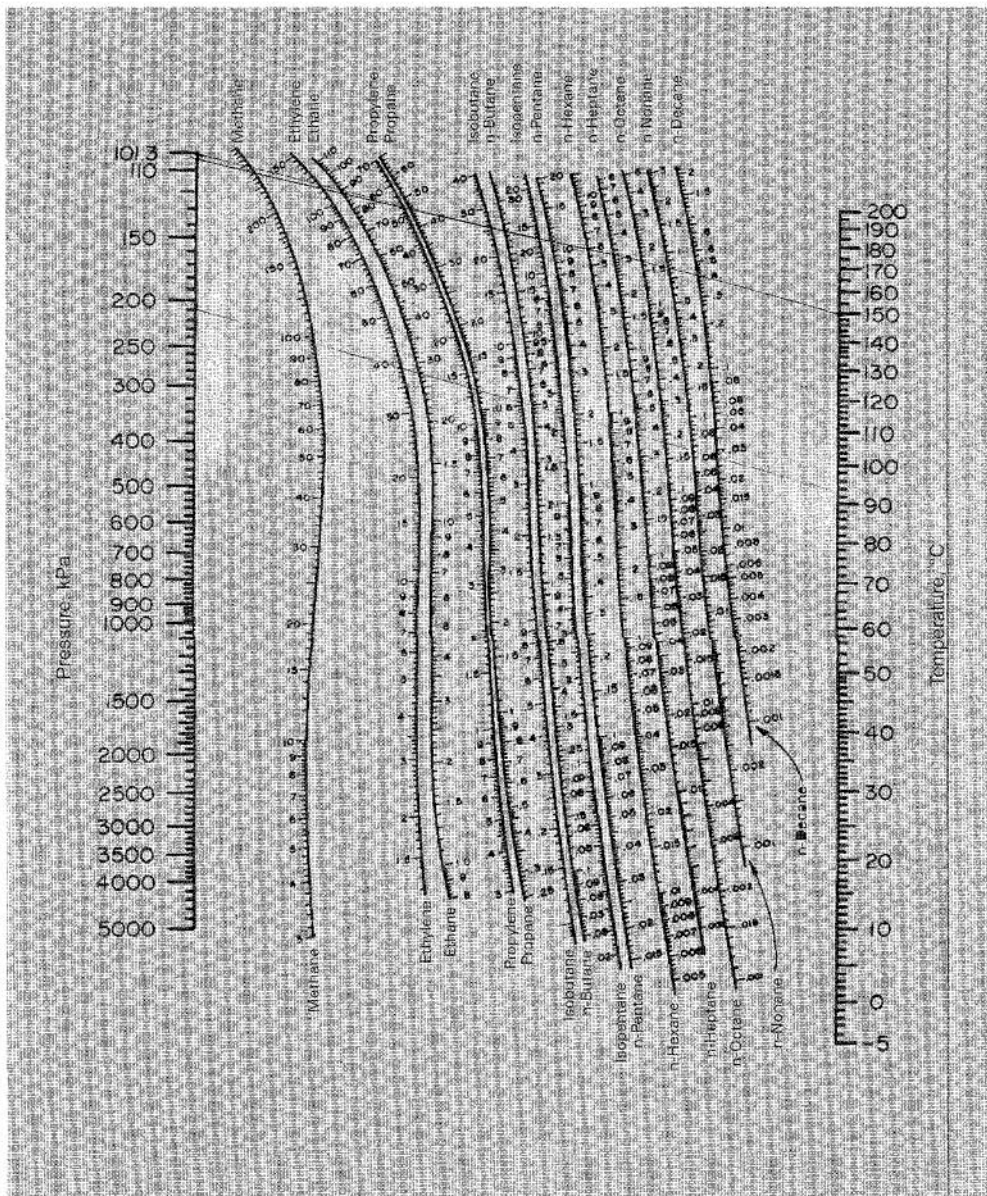
Solution 10.4

(a) When the system is at its dewpoint, only an insignificant amount of liquid is present, and the given mole fractions are values of y_i. For the given temperature, the K-values depend on the choice of P, and by trial we find the value for which Eq. (10.14) is satisfied. Results for several values of P are given as follows:

Species	y_i	$P = 6.9$ bar		$P = 10.34$ bar		$P = 8.7$ bar	
		K_i	y_i/K_i	K_i	y_i/K_i	K_i	y_i/K_i
Methane	0.10	20.0	0.005	13.2	0.008	16.0	0.006
Ethane	0.20	3.25	0.062	2.25	0.089	2.65	0.075
Propane	0.70	0.92	0.761	0.65	1.077	0.762	0.919
			$\Sigma(y_i/K_i) = 0.828$		$\Sigma(y_i/K_i) = 1.174$		$\Sigma(y_i/K_i) = 1.000$

The results given in the last two columns show that Eq. (10.14) is satisfied when $P = 8.7$ bar. This is the dewpoint pressure, and the composition of the dew is given by the values of $x_i = y_i/K_i$ listed in the last column of the table.

(b) When the system is almost completely condensed, it is at its bubblepoint, and the given mole fractions become values of x_i. In this case we find by trial the value of P for which the K-values satisfy Eq. (10.13). Results for several values of P are given in the following table:

Species	x_i	$P = 26.2$ bar		$P = 27.6$ bar		$P = 26.54$ bar	
		K_i	$K_i x_i$	K_i	$K_i x_i$	K_i	$K_i x_i$
Methane	0.10	5.60	0.560	5.25	0.525	5.49	0.549
Ethane	0.20	1.11	0.222	1.07	0.214	1.10	0.220
Propane	0.70	0.335	0.235	0.32	0.224	0.33	0.231
			$\Sigma K_i x_i = 1.017$		$\Sigma K_i x_i = 0.963$		$\Sigma K_i x_i = 1.000$

Equation (10.13) is satisfied when $P = 26.54$ bar. This is the bubblepoint pressure. The composition of the bubble of vapor is given by $y_i = K_i x_i$, as shown in the last column.

Flash Calculations

An important application of VLE is the *flash* calculation. The name originates from the fact that a liquid at a pressure equal to or greater than its bubblepoint pressure "flashes" or partially evaporates when the pressure is reduced, producing a two-phase system of vapor and liquid in equilibrium. We consider here only the P, T-flash, which refers to any calculation of the quantities and compositions of the vapor and liquid phases making up a two-phase system in equilibrium at known T, P, and overall composition. This poses a problem known to be

determinate on the basis of Duhem's theorem, because two independent variables (T and P) are specified for a system of fixed overall composition, that is, a system formed from given masses of nonreacting chemical species.

Consider a system containing one mole of nonreacting chemical species with an *overall* composition represented by the set of mole fractions $\{z_i\}$. Let $\mathcal{L}$ be the moles of liquid, with mole fractions $\{x_i\}$, and let $\mathcal{V}$ be the moles of vapor, with mole fractions $\{y_i\}$. The material-balance equations are:

$$\mathcal{L} + \mathcal{V} = 1$$

$$z_i = x_i \mathcal{L} + y_i \mathcal{V} \qquad (i = 1, 2, \ldots, N)$$

Combining these equations to eliminate $\mathcal{L}$ gives:

$$z_i = x_i(1 - \mathcal{V}) + y_i \mathcal{V} \qquad (i = 1, 2, \ldots, N) \tag{10.15}$$

Substituting $x_i = y_i / K_i$, and solving for y_i yields:

$$y_i = \frac{z_i K_i}{1 + \mathcal{V}(K_i - 1)} \qquad (i = 1, 2, \ldots, N) \tag{10.16}$$

Since $\sum_i y_i = 1$, Eq. *(10.16)* is summed over all species:

$$\sum_i \frac{z_i K_i}{1 + \mathcal{V}(K_i - 1)} = 1 \tag{10.17}$$

The initial step in solving a P, T-flash problem is to find the value of $\mathcal{V}$ which satisfies this equation. Note that $\mathcal{V} = 1$ is always a trivial solution.

Example 10.5

The system acetone(1)/acetonitrile(2)/nitromethane(3) at 353.15 K (80°C) and 110 kPa has the overall composition, $z_1 = 0.45$, $z_2 = 0.35$, $z_3 = 0.20$. Assuming that Raoult's law is appropriate to this system, determine $\mathcal{L}$, $\mathcal{V}$, $\{x_i\}$, and $\{y_i\}$. The vapor pressures of the pure species at 353.15 K (80°C) are:

$$P_1^{sat} = 195.75 \qquad P_2^{sat} = 97.84 \qquad P_3^{sat} = 50.32 \text{ kPa}$$

Solution 10.5

First, do a *BUBL P* calculation with $\{z_i\} = \{x_i\}$ to determine P_{bubl}. By Eq. (10.2),

$$P_{bubl} = x_1 P_1^{sat} + x_2 P_2^{sat} + x_3 P_3^{sat}$$

$$= (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) = 132.40 \text{ kPa}$$

Second, do a *DEW P* calculation with $\{z_i\} = \{y_i\}$ to find P_{dew}. By Eq. (10.3),

$$P_{dew} = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat} + y_3/P_3^{sat}} = 101.52 \text{ kPa}$$

Since the given pressure lies between P_{bubl} and P_{dew}, the system is in the two-phase region, and a flash calculation can be made.

By Eq. (10.11), $K_i = P_i^{sat}/P$; whence,

$$K_1 = 1.7795 \qquad K_2 = 0.8895 \qquad K_3 = 0.4575$$

Substitute known values into Eq. (10.17):

$$\frac{(0.45)(1.7795)}{1 + 0.7795\mathcal{V}} + \frac{(0.35)(0.8895)}{1 - 0.1105\mathcal{V}} + \frac{(0.20)(0.4575)}{1 - 0.5425\mathcal{V}} = 1 \qquad (A)$$

Solution for $\mathcal{V}$ by trial yields:

$$\mathcal{V} = 0.7364 \text{ mol}$$

Whence, $\qquad\qquad\qquad \mathcal{L} = 1 - \mathcal{V} = 0.2636 \text{ mol}$

Equation (10.16) shows that each term on the left side of Eq. (A) is an expression for y_i. Evaluation of these terms gives:

$$y_1 = 0.5087 \qquad y_2 = 0.3389 \qquad y_3 = 0.1524$$

Then by Eq. (10.10), $x_i = y_i/K_i$; whence,

$$x_1 = 0.2859 \qquad x_2 = 0.3810 \qquad x_3 = 0.3331$$

Obviously, $\sum_i y_i = \sum_i x_i = 1$. The procedure of this example is valid regardless of the number of species present.

Flash calculations can also be made for light hydrocarbons with the data of Figs. 10.13 and 10.14. The procedure here is exactly as described in Ex. 10.5, where Raoult's law applied. With T and P specified, the K-values for light hydrocarbons as given by Figs. 10.13 and 10.14 are known, and V, the only unknown in Eq. (10.17), is found by trial.

Example 10.6

For the system described in Ex. 10.4, what fraction of the system is vapor when the pressure is 13.8 bar and what are the compositions of the equilibrium vapor and liquid phases?

Solution 10.6

The given pressure lies between the dewpoint and bubblepoint pressures established for this system in Ex. 10.4. The system therefore consists of two phases. With K-values from Fig. 10.13, the procedure is to find by trial that value of $\mathcal{V}$ for which Eq. (10.17) is satisfied. The results of several trials are shown in the accompanying table. The columns headed y_i give values of the terms in the sum of Eq. (10.17), because each such term is in fact a y_i value.

Species	z_i	K_i	y_i for $V = 0.35$	y_i for $V = 0.25$	y_i for $V = 0.273$	$x_i = y_i/K_i$ for $V = 0.273$
Methane	0.10	10.0	0.241	0.308	0.289	0.029
Ethane	0.20	1.76	0.278	0.296	0.292	0.166
Propane	0.70	0.52	0.438	0.414	0.419	0.805
			$\Sigma y_i = 0.957$	$\Sigma y_i = 1.018$	$\Sigma y_i = 1.000$	$\Sigma x_i = 1.000$

Thus Eq. (10.17) is satisfied when $V = 0.273$. The phase compositions are given in the last two columns of the table.

PROBLEMS

Solutions to some of the problems of this chapter require vapor pressures as a function of temperature for species which constitute systems in VLE. Table 10.2 lists parameter values for the Antoine equation,

$$\ln P^{\text{sat}}/\text{kPa} = A - \frac{B}{T + C}$$

Table 10.2 Parameters for the Antoine Equation

	A	B	C
Acetone	14.3916	2795.82	−43.15
Acetonitrile	14.7258	3271.24	−31.30
Benzene	13.8594	2773.78	−53.08
Chlorobenzene	13.9926	3295.12	−55.60
1-Chlorobutane	13.9600	2826.26	−49.05
1,4-Dioxane	14.1177	2966.88	−63.15
Ethanol	16.6758	3674.49	−46.70
Ethylbenzene	14.0045	3279.47	−59.95
n-Heptane	13.8587	2991.32	−56.51
Methanol	16.5938	3644.30	−33.39
Methyl acetate	14.4015	2739.17	−50.03
n-Pentane	13.8183	2477.07	−39.94
1-Propanol	16.0692	3448.66	−69.06
Toluene	14.0098	3103.01	−53.36
Water	16.2620	3799.89	−46.80

10.1. Assuming the validity of Raoult's law, do the following calculations for the benzene(1)/toluene(2) system:
  (a) Given $x_1 = 0.33$ and $T = 373.15$ K $(100)°$C, find y_1 and P.
  (b) Given $y_1 = 0.33$ and $T = 373.15$ K $(100)°$C, find x_1 and P.

(c) Given $x_1 = 0.33$ and $P = 120$ kPa, find y_1 and T.

(d) Given $y_1 = 0.33$ and $P = 120$ kPa, find x_1 and T.

(e) Given T = 387.15 K (105°C) and $P = 120$ kPa, find x_1 and y_1.

(f) For part (e), if the overall mole fraction of benzene is $z_1 = 0.33$, what molar fraction of the two-phase system is vapor?

(g) Why is Raoult's law likely to be an excellent VLE model for this system at the stated (or computed) conditions?

10.2. Assuming Raoult's law to be valid, prepare a P-x-y diagram for a temperature of 363.15 K (90°C) and a t-x-y diagram for a pressure of 90 kPa for one of the following systems:

(a) Benzene(1)/ethylbenzene(2); (b) 1-Chlorobutane(1)/chlorobenzene(2).

10.3. Assuming Raoult's law to apply to the system n-pentane(1)/n-heptane(2),

(a) What are the values of x_1 and y_1 at T = 328.15 K (55°C) and $P = \frac{1}{2}(P_1^{sat} + P_2^{sat})$? For these conditions plot the fraction of system that is vapor V vs. overall composition z_1.

(b) For T = 328.15 K (55°C) and $z_1 = 0.5$, plot P, x_1, and y_1 vs. V.

10.4. Rework Pb. 10.3 for one of the following:

(a) T = 338.15 K (65°C); (b) T = 348.15 K (75°C); (c) T = 358.15 K (85°C); (d) T = 368.15 K (95°C).

10.5. Prove: An equilibrium liquidlvapor system described by Raoult's law cannot exhibit an azeotrope.

10.6. Of the binary liquid/vapor systems following, which can be approximately modeled by Raoult's law? For those which cannot, why? Table B.1 (App. B) may be useful.

(a) Benzeneltoluene at 1 atm.

(b) n-Hexaneln-heptane at 25 bar.

(c) Hydrogen/propane at 200 K.

(d) Isooctane/n-octane at 373.15 K (100°C).

(e) Waterln-decaneat 1 bar.

10.7. A single-stage liquid/vapor separation for the benzene(1)/ethylbenzene(2) system must produce phases of the following equilibrium compositions. For one of these sets, determine the T and P in the separator. What additional information is needed to compute the relative amounts of liquid and vapor leaving the separator? Assume that Raoult's law applies.

(a) $x_1 = 0.35$, $y_1 = 0.70$.

(b) $x_1 = 0.35$, $y_1 = 0.725$.

(c) $x_1 = 0.35$, $y_1 = 0.75$.

(d) $x_1 = 0.35$, $y_1 = 0.775$.

10.8. Do all four parts of Pb. 10.7, and compare the results. The required temperatures and pressures vary significantly. Discuss possible processing implications of the various temperature and pressure levels.

10.9. A mixture containing equimolar amounts of benzene(1), toluene(2), and ethylbenzene(3) is flashed to conditions T and P. For one of the conditions following determine the

equilibrium mole fractions $\{x_i\}$ and $\{y_i\}$ of the liquid and vapor phases formed and the molar fraction V of the vapor formed. Assume that Raoult's law applies.

(a) T $= 383.15$ K (110°C), $P = 90$ kPa.
(b) $T = 383.15$ K (110°C), $P = 100$ kPa.
(c) $T = 383.15$ K (110°C), $P = 110$ kPa.
(d) $T = 383.15$ K (110°C), $P = 120$ kPa.

10.10. Do all four parts of Pb. *10.9,* and compare the results. Discuss any trends that appear.

10.11. A binary mixture of mole fraction z_1 is flashed to conditions T and P. For one of the following determine: the equilibrium mole fractions x_1 and y_1 of the liquid and vapor phases formed, the molar fraction V of the vapor formed, and the fractional recovery $\mathcal{R}$ of species *1* in the vapor phase (defined as the ratio for species *1* of moles in the vapor to moles in the feed). Assume that Raoult's law applies.

(a) Acetone(1)/acetonitrile(2), $z_1 = 0.75$, $T = 340$ K, $P = 115$ kPa.
(b) Benzene(1)/ethylbenzene(2), $z_1 = 0.50$, $T = 373.15$ K (100°C), $P = 0.75$ atm.
(c) Ethanol(1)/1-propanol(2), $z_1 = 0.25$, $T = 360$ K, $P = 0.80$ atm.
(d) 1-Chlorobutane(1)/chlorobenzene(2), $z_1 = 0.50$, $T = 398.15$ K (125°C), $P = 1.75$ bar.

10.12. Humidity, relating to the quantity of moisture in atmospheric air, is accurately given by equations derived from the ideal-gas law and Raoult's law for H_2O.

(a) The *absolute humidity h* is defined as the mass of water vapor in a unit mass of dry air. Show that it is given by:

$$h = \frac{\mathcal{M}_{H_2O}}{\mathcal{M}_{air}} \frac{p_{H_2O}}{P - p_{H_2O}}$$

where $\mathbf{M}$ represents a molar mass and p_{H_2O} is the partial pressure of the water vapor, i.e., $p_{H_2O} = y_{H_2O} P$.

(b) The *saturation humidity h^{sat}* is defined as the value of h when air is in equilibrium with a large body of pure water. Show that it is given by:

$$h^{sat} = \frac{\mathcal{M}_{H_2O}}{\mathcal{M}_{air}} \frac{P_{H_2O}^{sat}}{P - P_{H_2O}^{sat}}$$

where $P_{H_2O}^{sat}$ is the vapor pressure of water at the ambient temperature.

(c) The *percentage humidity* is defined as the ratio of h to its saturation value, expressed as a percentage. On the other hand, the *relative humidity* is defined as the ratio of the partial pressure of water vapor in air to its vapor pressure, expressed as a percentage. What is the relation between these two quantities?

10.13. A concentrated binary solution containing mostly species 2 (but $x_2 \,\#\, 1$) is in equilibrium with a vapor phase containing both species *1* and *2*. The pressure of this two-phase system is *1* bar; the temperature is *298.15* K *(25°C).* Determine from the following data good estimates of x_1 and y_1.

$$\mathcal{H}_1 = 200 \text{ bar} \qquad P_2^{sat} = 0.10 \text{ bar}$$

State and justify all assumptions.

10.14. Air, even more so than carbon dioxide, is inexpensive and nontoxic. Why is it not the gas of choice for making soda water and (cheap) champagne effervescent? Table *10.1* may provide useful data.

10.15. Helium-laced gases are used as breathing media for deep-sea divers. Why? Table *10.1* may provide useful data.

10.16. A binary system of species *1* and *2* consists of vapor and liquid phases in equilibrium at temperature T. The *overall* mole fraction of species 1 in the system is $z_1 = 0.65$. At temperature T,

- $\ln \gamma_1 = 0.67 x_2^2$ $\ln \gamma_2 = 0.67 x_1^2$.
- $P_1^{\text{sat}} = 32.27$ kPa $P_2^{\text{sat}} = 73.14$ kPa.

Assuming the validity of Eq. (10.5),

(*a*) Over what range of pressures can this system exist as two phases at given T and z_1?

(*b*) For a liquid-phase mole fraction $x_1 = 0.75$, what is the pressure P and what molar fraction V of the system is vapor?

(*c*) Show whether or not the system exhibits an azeotrope.

10.17. For the system ethyl ethanoate(1)/*n*-heptane(2) at *343.15* K (70°C),

- $\ln \gamma_1 = 0.95 x_2^2$ $\ln \gamma_2 = 0.95 x_1^2$.
- $P_1^{\text{sat}} = 79.80$ kPa $P_2^{\text{sat}} = 40.50$ kPa.

Assuming the validity of Eq. (10.5),

(*a*) Make a *BUBL* P calculation for T $= 343.15$ K (70°C), $x_1 = 0.05$.

(*b*) Make a *DEW* P calculation for $T = 343.15$ K (70°C), $y_1 = 0.05$.

(*c*) What is the azeotrope composition and pressure at T $= 343.15$ K (70°C)?

10.18. A liquid mixture of cyclohexanone(1)/phenol(2) for which $x_1 = 0.6$ is in equilibrium with its vapor at *417.15* K *(144°C)*. Determine the equilibrium pressure P and vapor composition y_1 from the following information:

- $\ln \gamma_1 = A x_2^2$ $\ln \gamma_2 = A x_1^2$.
- At *417.15* K (144°C), $P_1^{\text{sat}} = 75.20$ and $P_2^{\text{sat}} = 31.66$ kPa.
- The system forms an azeotrope at *417.15* K *(144°C)* for which $x_1^{\text{az}} = y_1^{\text{az}} = 0.294$.

10.19. A binary system of species *1* and 2 consists of vapor and liquid phases in equilibrium at temperature T, for which

- $\ln \gamma_1 = 1.8 x_2^2$ $\ln \gamma_2 = 1.8 x_1^2$.
- $P_1^{\text{sat}} = 1.24$ bar $P_2^{\text{sat}} = 0.89$ bar.

Assuming the validity of Eq. (10.5),

(*a*) For what range of values of the *overall* mole fraction z_1 can this two-phase system exist with a *liquid* mole fraction $x_1 = 0.65$?

(b) What is the pressure P and vapor mole fraction y_1 within this range?

(*c*) What are the pressure and composition of the azeotrope at temperature T?

10.20. For the acetone(1)/methanol(2) system a vapor mixture for which $z_1 = 0.25$ and $z_2 = 0.75$ is cooled to temperature T in the two-phase region and flows into a separation chamber at a pressure of 1 bar. If the composition of the liquid product is to be $x_1 = 0.175$, what is the required value of T, and what is the value of y_1? For liquid mixtures of this system to a good approximation:

$$\ln \gamma_1 = 0.64 x_2^2 \qquad\qquad \ln \gamma_2 = 0.64 x_1^2$$

10.21. The following is a rule of thumb: For a binary system in VLE at low pressure, the equilibrium vapor-phase mole fraction y_1 corresponding to an equimolar liquid mixture is approximately

$$y_1 = \frac{P_1^{\text{sat}}}{P_1^{\text{sat}} + P_2^{\text{sat}}}$$

where P_i^{sat} is a pure-species vapor pressure. Clearly, this equation is valid if Raoult's law applies. Prove that it is also valid for VLE described by Eq. (10.5), with:

$$\ln \gamma_1 = A x_2^2 \qquad\qquad \ln \gamma_2 = A x_1^2$$

10.22. A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is desired, obtained by a single-stage liquid/vapor separation. Specifications on the equilibrium composition are: $x_1 = 0.002$ and $y_1 = 0.950$. Use data given below to determine $T(\text{K})$ and $P(\text{bar})$ for the separator. Assume that Eq. (10.5) applies; the calculated P should validate this assumption. Data:

For the liquid phase, $\ln \gamma_1 = 0.93 x_2^2 \qquad \ln \gamma_2 = 0.93 x_1^2$

$$\ln P_i^{\text{sat}}/\text{bar} = A_i - \frac{B_i}{T/\text{K}}$$

$$A_1 = 10.08,\ B_1 = 2572.0,\ A_2 = 11.63,\ B_2 = 6254.0$$

10.23. If a system exhibits VLE, at least one of the K-values must be greater than 1.0 and at least one must be less than 1.0. Offer a proof of this observation.

10.24. Flash calculations are simpler for binary systems than for the general multicomponent case, because the equilibrium compositions for a binary are independent of the overall composition. Show that, for a binary system in VLE,

$$x_1 = \frac{1 - K_2}{K_1 - K_2} \qquad\qquad y_1 = \frac{K_1(1 - K_2)}{K_1 - K_2}$$

$$\mathcal{V} = \frac{z_1(K_1 - K_2) - (1 - K_2)}{(K_1 - 1)(1 - K_2)}$$

10.25. Assuming the validity of the Dadyburjor charts (Fig. 10.13 and 10.14), make the following VLE calculations for the methane(1)/ethylene(2)/ethane(3) system:

(a) *BUBL* P, given $x_1 = 0.10$, $x_2 = 0.50$, and T $= 222.15$ K (-51°C).
(b) *DEW* P, given $y_1 = 0.50$, $y_2 = 0.25$, and T $= 222.15$ K (-51°C).
(c) *BUBL T*, given $x_1 = 0.12$, $x_2 = 0.40$, and $P = 17.24$ bar.
(d) *DEW* T, given $y_1 = 0.43$, $y_2 = 0.36$, and $P = 17.24$ bar.

10.26. Assuming the validity of the Dadyburjorcharts (Fig. 10.13 and 10.14), make the following VLE calculations for the ethane(1)/propane(2)/isobutane(3)/isopentane(4) system:

(a) BUBL P, given $x_1 = 0.10$, $x_2 = 0.20$, $x_3 = 0.30$, and $t = 333.15$ K (60°C).

(b) *DEW* P, given $y_1 = 0.48$, $y_2 = 0.25$, $y_3 = 0.15$, and $t = 333.15$ K (60°C).

(c) *BUBL T*, $x_1 = 0.14$, $x_2 = 0.13$, $x_3 = 0.25$, and $P = 15$ bar.

(d) *DEW T*, given $y_1 = 0.42$, $y_2 = 0.30$, $y_3 = 0.15$, and $P = 15$ bar.

10.27. The stream from a gas well is a mixture containing 50-mol-% methane, 10-mol-% ethane, 20-mol-% propane, and 20-mol-% n-butane. This stream is fed into a partial condenser maintained at a pressure of 17.24 bar, where its temperature is brought to 300.15 K (27°C). Determine the molar fraction of the gas that condenses and the compositions of the liquid and vapor phases leaving the condenser.

10.28. An equimolar mixture of n-butane and n-hexane at pressure P is brought to a temperature of 368.15 K (95°C), where it exists as a vaporlliquid mixture in equilibrium. If the mole fraction of n-hexane in the liquid phase is 0.75, what is pressure P (in bar), what is the molar fraction of the system that is liquid, and what is the composition of the vapor phase?

10.29. A mixture— 25-mol-% n-pentane, 45-mol-% n-hexane, and 30-mol-% n-heptane — is brought to a condition of 366.15 K (93°C) and 2 atm. What molar fraction of the system is liquid, and what are the phase compositions?

10.30. A mixture containing 15-mol-% ethane, 35-mol-% propane, and 50-mol-% n-butane is brought to a condition of 313.15 K (40°C) at pressure P. If the molar fraction of liquid in the system is 0.40, what is pressure P (in bar) and what are the compositions of the liquid and vapor phases?

10.31. A mixture consisting of 1-mol-% ethane, 5-mol-% propane, 44-mol-% n-butane, and 50-mol-% isobutane is brought to a condition of 294.15 K (21°C) at pressure P. If the molar fraction of the system that is vapor is 0.2, what is pressure P (in bar), and what are the compositions of the vapor and liquid phases?

10.32. A mixture comprised of 30-mol-% methane, 10-mol-% ethane, 30-mol-% propane, and 30-mol-% n-butane is brought to a condition of 258.15 K (−15°C) at pressure P, where it exists as a vaporlliquid mixture in equilibrium. If the mole fraction of the methane in the vapor phase is 0.80, what is pressure P (in bar)?

10.33. The top tray of a distillation column and the condenser are at a pressure of 1.38 bar. The liquid on the top tray is an equimolar mixture of n-butane and n-pentane. The vapor from the top tray, assumed to be in equilibrium with the liquid, goes to the condenser where 50 mol-% of the vapor is condensed. What is the temperature on the top tray? What are the temperature and composition of the vapor leaving the condenser?

10.34. n-Butane is separatedfrom an equimolar methaneln-butanegas mixture by compression of the gas to pressure P at 313.15 K (40°C). If 40% of the feed on a mole basis is condensed, what is pressure P (in bar) and what are the compositions of the resulting vapor and liquid phases?