

# Chapter 4

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## Single Equilibrium Stages and Flash Calculations

### §4.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Explain what an equilibrium stage is and why it may not be sufficient to achieve a desired separation.
- Extend Gibbs phase rule to include extensive variables so that the number of degrees of freedom (number of variables minus the number of independent relations among the variables) can be determined.
- Use  $T$ - $y$ - $x$  and  $y$ - $x$  diagrams of binary mixtures, with the  $q$ -line, to determine equilibrium compositions.
- Understand the difference between minimum- and maximum-boiling azeotropes and how they form.
- Calculate bubble-point, dew-point, and equilibrium-flash conditions.
- Use triangular phase diagrams for ternary systems with component material balances to determine equilibrium compositions of liquid–liquid mixtures.
- Use distribution (partition) coefficients, from activity coefficients, with component material-balance equations to calculate liquid–liquid phase equilibria for multicomponent systems.
- Use equilibrium diagrams with material balances to determine amounts and compositions for solid–fluid systems (leaching, crystallization, sublimation, desublimation, adsorption) and gas absorption in liquids.

The simplest separation process is one in which two phases in contact are brought to physical equilibrium, followed by phase separation. If the separation factor, Eq. (1-4), between two species in the two phases is very large, a single contacting stage may be sufficient to achieve a desired separation between them; if not, multiple stages are required. For example, if a vapor phase is brought to equilibrium with a liquid phase, the separation factor is the relative volatility,  $\alpha$ , of a volatile component called the light key, LK, with respect to a less-volatile component called the heavy key, HK, where  $\alpha_{LK, HK} = K_{LK}/K_{HK}$ . If the separation factor is 10,000, a near-perfect separation is achieved in a single equilibrium stage. If the separation factor is only 1.10, an almost perfect separation requires hundreds of equilibrium stages.

In this chapter, only a single equilibrium stage is considered, but a wide spectrum of separation operations is described. In all cases, a calculation is made by combining material balances with phase-equilibrium relations discussed in Chapter 2. When a phase change such as vaporization occurs, or when heat of mixing effects are large, an energy balance must be added to account for a temperature change. The next chapter describes arrangements of multiple equilibrium stages, called cascades, which are used when the desired degree of separation cannot be achieved with a single stage. The specification of both single-stage and multiple-stage separation operations, is not intuitive. For that reason,

this chapter begins with a discussion of Gibbs phase rule and its extension to batch and continuous operations.

Although not always stated, all diagrams and most equations in this chapter are valid only if the phases are at equilibrium. If mass-transfer rates are too slow, or if the time to achieve equilibrium is longer than the contact time, the degree of separation will be less than calculated by the methods in this chapter. In that case, stage efficiencies must be introduced into the equations, as discussed in Chapter 6, or calculations must be based on mass-transfer rates rather than phase equilibrium, as discussed in Chapter 12.

### §4.1 GIBBS PHASE RULE AND DEGREES OF FREEDOM

Equilibrium calculations involve *intensive variables*, which are independent of quantity, and *extensive variables*, which depend on quantity. Temperature, pressure, and mole or mass fractions are intensive. Extensive variables include mass or moles and energy for a batch system, and mass or molar flow rates and energy-transfer rates for a flow system.

Phase-equilibrium equations, and mass and energy balances, provide dependencies among the intensive and extensive variables. When a certain number of the variables (called the independent variables) are specified, all other variables (called the dependent variables) become fixed. The number

of independent variables is called the *variance*, or the number of *degrees of freedom*,  $\mathcal{F}$ .

### §4.1.1 Gibbs Phase Rule

At physical equilibrium and when only intensive variables are considered, the Gibbs phase rule applies for determining  $\mathcal{F}$ . The rule states that

$$\mathcal{F} = C - \mathcal{P} + 2 \quad (4-1)$$

where  $C$  is the number of components and  $\mathcal{P}$  is the number of phases. Equation (4-1) is derived by counting the number of intensive variables,  $\mathcal{V}$ , and the number of independent equations,  $\mathcal{E}$ , that relate these variables. The number of intensive variables is

$$\mathcal{V} = C\mathcal{P} + 2 \quad (4-2)$$

where the 2 refers to temperature and pressure, and  $C\mathcal{P}$  is the total number of composition variables (e.g., mole fractions) for components distributed among  $\mathcal{P}$  phases. The number of independent equations relating the intensive variables is

$$\mathcal{E} = \mathcal{P} + C(\mathcal{P} - 1) \quad (4-3)$$

where the first term,  $\mathcal{P}$ , refers to the requirement that mole fractions sum to one in each phase, and the second term,  $C(\mathcal{P} - 1)$ , refers to the number of independent phase-equilibrium equations of the form

$$K_i = \frac{\text{mole fraction of } i \text{ in phase (1)}}{\text{mole fraction of } i \text{ in phase (2)}}$$

where (1) and (2) refer to equilibrium phases. For two phases, there are  $C$  independent expressions of this type; for three phases,  $2C$ ; for four phases,  $3C$ ; and so on. For example, for three phases ( $V$ ,  $L^{(1)}$ ,  $L^{(2)}$ ), there are  $3C$  different  $K$ -value equations:

$$\begin{aligned} K_i^{(1)} &= y_i/x_i^{(1)} & i &= 1 \text{ to } C \\ K_i^{(2)} &= y_i/x_i^{(2)} & i &= 1 \text{ to } C \\ K_{D_i} &= x_i^{(1)}/x_i^{(2)} & i &= 1 \text{ to } C \end{aligned}$$

However, **only 2C of these equations are independent**, because

$$K_{D_i} = K_i^{(2)}/K_i^{(1)}$$

Thus, the number of independent  $K$ -value equations is

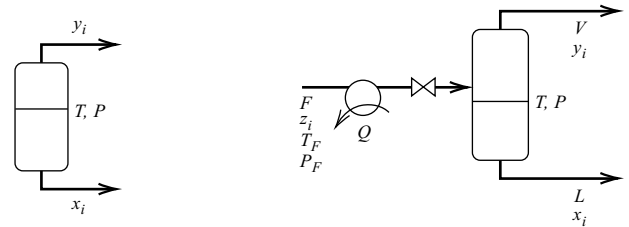
$$C(\mathcal{P} - 1), \text{ and not } C\mathcal{P}$$

The degrees of freedom for Gibbs phase rule is the number of intensive variables,  $\mathcal{V}$ , less the number of independent equations,  $\mathcal{E}$ . Thus, from (4-2) and (4-3), (4-1) is derived:

$$\mathcal{F} = \mathcal{V} - \mathcal{E} = (C\mathcal{P} + 2) - [\mathcal{P} + C(\mathcal{P} - 1)] = C - \mathcal{P} + 2$$

If  $\mathcal{F}$  intensive variables are specified, the remaining  $\mathcal{P} + C(\mathcal{P} - 1)$  intensive variables are determined from  $\mathcal{P} + C(\mathcal{P} - 1)$  equations. In using the Gibbs phase rule, it should be noted that the  **$K$ -values are not counted as variables because they are thermodynamic functions that depend on the intensive variables.**

As an example of the application of the Gibbs phase rule, consider the vapor–liquid equilibrium ( $\mathcal{P} = 2$ ) in Figure



Independent equations:

$$\begin{aligned} \sum_{i=1}^C y_i &= 1 \\ \sum_{i=1}^C x_i &= 1 \\ K_i &= \frac{y_i}{x_i}, \quad i = 1 \text{ to } C \end{aligned}$$

(a)

Independent equations:

$$\begin{aligned} &\text{Same as for (a) plus} \\ Fz_i &= Vy_i + Lx_i \quad i = 1 \text{ to } C \\ Fh_F + Q &= Vh_V + Lh_L \end{aligned}$$

(b)

**Figure 4.1** Treatments of degrees of freedom for vapor–liquid phase equilibria: (a) Gibbs phase rule (considers intensive variables only); (b) general analysis (considers both intensive and extensive variables).

4.1a, where the intensive variables are labels on the sketch above the list of independent equations relating these variables. Suppose there are  $C = 3$  components. From (4-2) there are eight intensive variables:  $T$ ,  $P$ ,  $x_1$ ,  $x_2$ ,  $x_3$ ,  $y_1$ ,  $y_2$ , and  $y_3$ . From (4-1),  $\mathcal{F} = 3 - 2 + 2 = 3$ .

Suppose these three degrees of freedom are used to specify three variables:  $T$ ,  $P$ , and one mole fraction. From (4-3) there are five independent equations, listed in Figure 4.1a, which are then used to compute the remaining five mole fractions. Similarly, if the number of components were two instead of three, only two variables need be specified.

**Irrational specifications must be avoided because they lead to infeasible results.** For example, if the components are  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$ , and  $T = 100^\circ\text{F}$  and  $P = 15$  psia are specified, a specification of  $x_{\text{N}_2} = 0.90$  is not feasible because nitrogen is not this soluble.

### §4.1.2 Extension of Gibbs Phase Rule to Extensive Variables

The Gibbs phase rule is limited because it does not deal with the extensive variables of feed, product, and energy streams, whether for a batch or continuous process. However, the rule can be extended for process applications by adding material and energy streams, with their extensive variables (e.g., flow rates or amounts), and additional independent equations. To illustrate this, consider the continuous, single-stage ( $\mathcal{P} = 2$ ) process in Figure 4.1b. By comparison with Figure 4.1a, the additional variables are:  $z_i$ ,  $T_F$ ,  $P_F$ ,  $F$ ,  $Q$ ,  $V$ , and  $L$ , or  $C + 6$  additional variables, shown in the diagram of Figure 4.1a. In general, for  $\mathcal{P}$  phases, the additional variables number  $C + \mathcal{P} + 4$ . The additional independent equations, listed below Figure 4.1b, are the  $C$  component material balances and the energy balance, for a total of  $C + 1$  equations. Note that, like  $K$ -values, stream enthalpies are not counted as variables.

For a degrees-of-freedom analysis for phase equilibrium involving one feed phase,  $\mathcal{P}$  product phases, and  $C$  components, (4-2) and (4-3) are extended by adding the above increments as a number of additional variables and equations:

$$\begin{aligned}\mathcal{V} &= (C\mathcal{P} + 2) + (C + \mathcal{P} + 4) = \mathcal{P} + C\mathcal{P} + C + 6 \\ \mathcal{E} &= [\mathcal{P} + C(\mathcal{P} - 1)] + (C + 1) = \mathcal{P} + C\mathcal{P} + 1 \quad (4-4) \\ \mathcal{F} &= \mathcal{V} - \mathcal{E} = C + 5\end{aligned}$$

If the  $C + 5$  degrees of freedom are used to specify all  $z_i$  and the five variables  $F$ ,  $T_F$ ,  $P_F$ ,  $T$ , and  $P$ , the remaining variables are found using equations in Figure 4.1.<sup>1</sup> When applying (4-4), determination of the number of phases,  $\mathcal{P}$ , is implicit in the computational procedure as illustrated later in this chapter.

Next, the Gibbs phase rule, (4-1), and the equation for the degrees of freedom of a flow system, (4-4), are applied to (1) tabular equilibrium data, (2) graphical equilibrium data, and (3) thermodynamic equations for  $K$ -values and enthalpies for multiphase systems.

## §4.2 BINARY VAPOR–LIQUID SYSTEMS

Experimental vapor–liquid equilibrium data for binary systems are widely available. Sources include *Perry's Handbook* [1], Gmehling and Onken [2], and Hála [3]. Because  $y_B = 1 - y_A$  and  $x_B = 1 - x_A$ , the data are presented in terms of just four intensive variables:  $T$ ,  $P$ ,  $y_A$ , and  $x_A$ . Most commonly  $T$ ,  $y_A$ , and  $x_A$  are tabulated at a fixed  $P$  for  $y_A$  and  $x_A$  from 0 to 1, where A is the more-volatile component ( $y_A > x_A$ ). However, if an azeotrope forms, B becomes the more-volatile component on one side of the azeotropic point.

By the Gibbs phase rule, (4-1),  $\mathcal{F} = 2 - 2 + 2 = 2$ . Thus, with pressure fixed, phase compositions are completely defined if temperature and the relative volatility, (4-5), are fixed.

$$\alpha_{A,B} = \frac{K_A}{K_B} = \frac{(y_A/x_A)}{(y_B/x_B)} = \frac{(y_A/x_A)}{(1 - y_A)/(1 - x_A)} \quad (4-5)$$

Equilibrium data of the form  $T$ – $y_A$ – $x_A$  at 1 atm for three binary systems of importance are given in Table 4.1. Included are values of relative volatility computed from (4-5).

As discussed in Chapter 2,  $\alpha_{A,B}$  depends on  $T$ ,  $P$ , and the phase compositions. At 1 atm, where  $\alpha_{A,B}$  is approximated well by  $\gamma_A^S P_A^S / \gamma_B^S P_B^S$ ,  $\alpha_{A,B}$  depends only on  $T$  and  $x_A$ , since vapor-phase nonidealities are small. Because  $\alpha_{A,B}$  depends on  $x_A$ , it is not constant. For the three binary systems in Table 4.1, at 1 atm pressure,  $T$ – $y_A$ – $x_A$  data are presented. Both phases become richer in the less-volatile component, B, as temperature increases. For  $x_A = 1$ , the temperature is the boiling point of A at 1 atm; for  $x_A = 0$ , the temperature is the normal boiling point of B. For the three systems, all other data points are at temperatures between the two boiling points. Except for the pure components ( $x_A = 1$  or 0),  $y_A > x_A$  and  $\alpha_{A,B} > 1$ .

<sup>1</sup>Development of (4-4) assumes that the sum of mole fractions in the feed equals one. Alternatively, the equation  $\sum_{i=1}^C z_i = 1$  can be added to the number of independent equations (thus forcing the feed mole fractions to sum to one). Then, the degrees of freedom becomes one less or  $C + 4$ .

**Table 4.1** Vapor–Liquid Equilibrium Data for Three Common Binary Systems at 1 atm Pressure

### a. Water (A)–Glycerol (B) System

$P = 101.3$  kPa

Data of Chen and Thompson, *J. Chem. Eng. Data*, **15**, 471 (1970)

| Temperature, °C | $y_A$  | $x_A$  | $\alpha_{A,B}$ |
|-----------------|--------|--------|----------------|
| 100.0           | 1.0000 | 1.0000 |                |
| 104.6           | 0.9996 | 0.8846 | 333            |
| 109.8           | 0.9991 | 0.7731 | 332            |
| 128.8           | 0.9980 | 0.4742 | 544            |
| 148.2           | 0.9964 | 0.3077 | 627            |
| 175.2           | 0.9898 | 0.1756 | 456            |
| 207.0           | 0.9804 | 0.0945 | 481            |
| 244.5           | 0.9341 | 0.0491 | 275            |
| 282.5           | 0.8308 | 0.0250 | 191            |
| 290.0           | 0.0000 | 0.0000 |                |

### b. Methanol (A)–Water (B) System

$P = 101.3$  kPa

Data of J.G. Dunlop, M.S. thesis, Brooklyn Polytechnic Institute (1948)

| Temperature, °C | $y_A$ | $x_A$ | $\alpha_{A,B}$ |
|-----------------|-------|-------|----------------|
| 64.5            | 1.000 | 1.000 |                |
| 66.0            | 0.958 | 0.900 | 2.53           |
| 69.3            | 0.870 | 0.700 | 2.87           |
| 73.1            | 0.779 | 0.500 | 3.52           |
| 78.0            | 0.665 | 0.300 | 4.63           |
| 84.4            | 0.517 | 0.150 | 6.07           |
| 89.3            | 0.365 | 0.080 | 6.61           |
| 93.5            | 0.230 | 0.040 | 7.17           |
| 100.0           | 0.000 | 0.000 |                |

### c. Para-xylene (A)–Meta-xylene (B) System

$P = 101.3$  kPa

Data of Kato, Sato, and Hirata, *J. Chem. Eng. Jpn.*, **4**, 305 (1970)

| Temperature, °C | $y_A$  | $x_A$  | $\alpha_{A,B}$ |
|-----------------|--------|--------|----------------|
| 138.335         | 1.0000 | 1.0000 |                |
| 138.491         | 0.8033 | 0.8000 | 1.0041         |
| 138.644         | 0.6049 | 0.6000 | 1.0082         |
| 138.795         | 0.4049 | 0.4000 | 1.0123         |
| 138.943         | 0.2032 | 0.2000 | 1.0160         |
| 139.088         | 0.0000 | 0.0000 |                |

For the water–glycerol system, the difference in boiling points is 190°C. Therefore, relative volatility values are very high, making it possible to achieve a good separation in a single equilibrium stage. Industrially, the separation is often conducted in an evaporator, which produces a nearly pure water vapor and a glycerol-rich liquid. For example, as seen in the Table 4.1a, at 207°C, a vapor of 98 mol% water is in equilibrium with a liquid containing more than 90 mol% glycerol.

For the methanol–water system, in Table 4.1b, the difference in boiling points is 35.5°C and the relative volatility is an order of magnitude lower than for the water–glycerol

system. A sharp separation cannot be made with a single stage. A 30-tray distillation column is required to obtain a 99 mol% methanol distillate and a 98 mol% water bottoms.

For the paraxylene–metaxylene isomer system in Table 4.1c, the boiling-point difference is only 0.8°C and the relative volatility is very close to 1.0, making separation by distillation impractical because about 1,000 trays are required to produce nearly pure products. Instead, crystallization and adsorption, which have much higher separation factors, are used commercially.

Vapor–liquid equilibrium data for methanol–water in Table 4.2 are in the form of  $P$ – $y_A$ – $x_A$  for temperatures of 50, 150, and 250°C. The data cover a wide pressure range of 1.789 to 1,234 psia, with temperatures increasing with pressure. At 50°C,  $\alpha_{AB}$  averages 4.94. At 150°C, the average  $\alpha_{AB}$  is only 3.22; and at 250°C, it is 1.75. Thus, as temperature and pressure increase,  $\alpha_{AB}$  decreases. For the data set at 250°C, it is seen that as compositions become richer in methanol, a point is reached near 1,219 psia, at a methanol mole fraction of 0.772, where the relative volatility is 1.0 and distillation is impossible because the vapor and liquid compositions are identical and the two phases become one. This is the critical point for the mixture. It is intermediate between the critical points of methanol and water:

| $y_A = x_A$ | $T_c, ^\circ\text{C}$ | $P_c, \text{psia}$ |
|-------------|-----------------------|--------------------|
| 0.000       | 374.1                 | 3,208              |
| 0.772       | 250                   | 1,219              |
| 1.000       | 240                   | 1,154              |

Critical conditions exist for each binary composition. In industry, distillation columns operate at pressures well below the critical pressure of the mixture to avoid relative volatilities that approach 1.

The data for the methanol–water system are plotted in three different ways in Figure 4.2: (a)  $T$  vs.  $y_A$  or  $x_A$  at  $P = 1$  atm; (b)  $y_A$  vs.  $x_A$  at  $P = 1$  atm; and (c)  $P$  vs.  $x_A$  at  $T = 150^\circ\text{C}$ . These plots satisfy the requirement of the Gibbs phase rule that when two intensive variables are fixed, all other variables are determined. Of the three diagrams in Figure 4.2, only (a) contains the complete data; (b) does not contain temperatures; and (c) does not contain vapor-phase mole fractions. Mass or mole fractions could be used, but the latter are preferred because vapor–liquid equilibrium relations are always based on molar properties.

Plots like Figure 4.2a are useful for determining phase states, phase-transition temperatures, phase compositions, and phase amounts. Consider the  $T$ – $y$ – $x$  plot in Figure 4.3 for the  $n$ -hexane (H)– $n$ -octane (O) system at 101.3 kPa.

The upper curve, labeled “Saturated vapor,” gives the dependency of vapor mole fraction on the dew-point temperature; the lower curve, labeled “Saturated liquid,” shows the bubble-point temperature as a function of liquid-phase mole fraction. The two curves converge at  $x_H = 0$ , the normal boiling point of  $n$ -octane (258.2°F), and at  $x_H = 1$ , the boiling point of normal hexane (155.7°F). For two phases to exist, a point representing the overall composition of the binary mixture at a given temperature must be located in the two-phase

**Table 4.2** Vapor–Liquid Equilibrium Data for the Methanol–Water System at Temperatures of 50, 150, and 250°C

**a. Methanol (A)–Water (B) System**

$T = 50^\circ\text{C}$

Data of McGlashan and Williamson, *J. Chem. Eng. Data*, **21**, 196 (1976)

| Pressure, psia | $y_A$  | $x_A$  | $\alpha_{A,B}$ |
|----------------|--------|--------|----------------|
| 1.789          | 0.0000 | 0.0000 |                |
| 2.373          | 0.2661 | 0.0453 | 7.64           |
| 3.369          | 0.5227 | 0.1387 | 6.80           |
| 4.641          | 0.7087 | 0.3137 | 5.32           |
| 5.771          | 0.8212 | 0.5411 | 3.90           |
| 6.811          | 0.9090 | 0.7598 | 3.16           |
| 7.800          | 0.9817 | 0.9514 | 2.74           |
| 8.072          | 1.0000 | 0.0000 |                |

**b. Methanol (A)–Water (B) System**

$T = 150^\circ\text{C}$

Data of Griswold and Wong, *Chem. Eng. Prog. Symp. Ser.*, **48**(3), 18 (1952)

| Pressure, psia | $y_A$ | $x_A$ | $\alpha_{A,B}$ |
|----------------|-------|-------|----------------|
| 73.3           | 0.060 | 0.009 | 7.03           |
| 85.7           | 0.213 | 0.044 | 5.88           |
| 93.9           | 0.286 | 0.079 | 4.67           |
| 139.7          | 0.610 | 0.374 | 2.62           |
| 160.4          | 0.731 | 0.578 | 1.98           |
| 193.5          | 0.929 | 0.893 | 1.57           |
| 196.5          | 0.960 | 0.936 | 1.64           |
| 199.2          | 0.982 | 0.969 | 1.75           |

**c. Methanol (A)–Water (B) System**

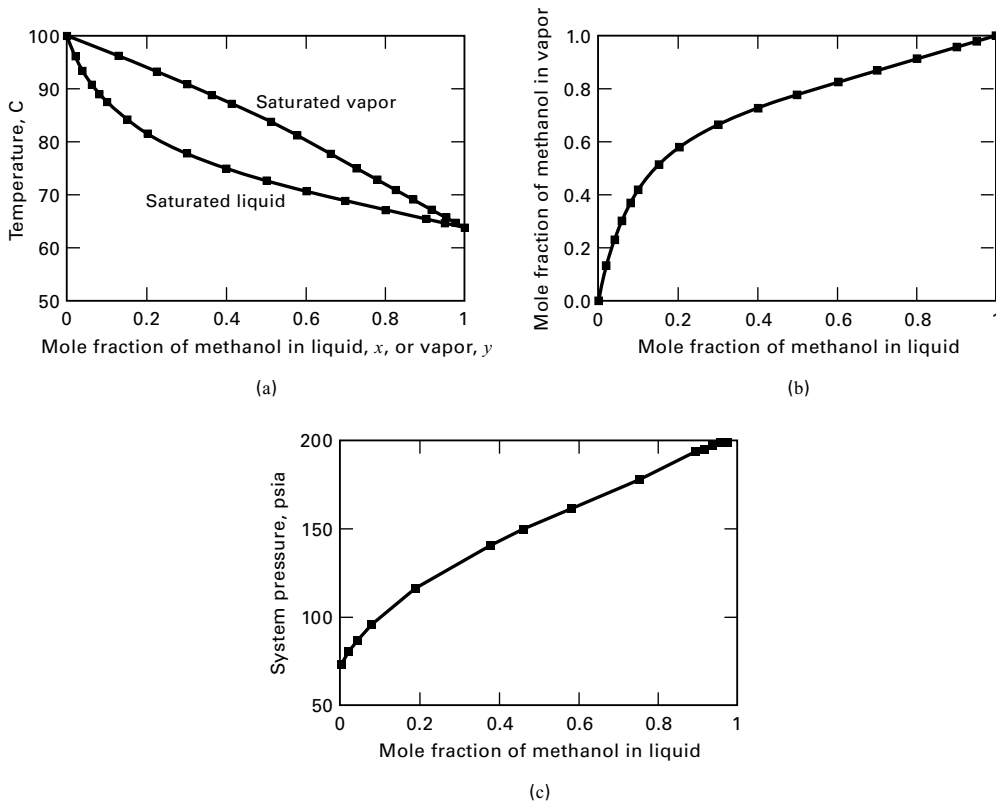
$T = 250^\circ\text{C}$

Data of Griswold and Wong, *Chem. Eng. Prog. Symp. Ser.*, **48**(3), 18 (1952)

| Pressure, psia | $y_A$ | $x_A$ | $\alpha_{A,B}$ |
|----------------|-------|-------|----------------|
| 681            | 0.163 | 0.066 | 2.76           |
| 818            | 0.344 | 0.180 | 2.39           |
| 949            | 0.487 | 0.331 | 1.92           |
| 1099           | 0.643 | 0.553 | 1.46           |
| 1204           | 0.756 | 0.732 | 1.13           |
| 1219           | 0.772 | 0.772 | 1.00           |
| 1234           | 0.797 | 0.797 | 1.00           |

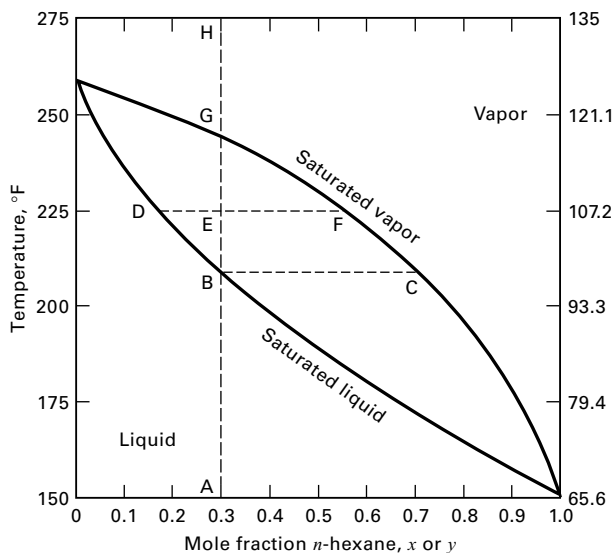
region between the two curves. If the point lies above the saturated-vapor curve, a superheated vapor exists; if the point lies below the saturated-liquid curve, a subcooled liquid exists.

Consider a mixture of 30 mol% H at 150°F. From Figure 4.3, point A is a subcooled liquid with  $x_H = 0.3$ . When this mixture is heated at 1 atm, it remains liquid until a temperature of 210°F, point B, is reached. This is the *bubble point* where the first bubble of vapor appears. This bubble is a saturated vapor in equilibrium with the liquid at the same



**Figure 4.2** Vapor–liquid equilibrium conditions for the methanol–water system: (a)  $T$ - $y$ - $x$  diagram for 1 atm pressure; (b)  $y$ - $x$  diagram for 1 atm pressure; (c)  $P$ - $x$  diagram for 150°C.

temperature. Its composition is determined by following a *tie line*, which in Figure 4.3 is BC, from  $x_H = 0.3$  to  $y_H = 0.7$ . This tie line is horizontal because the phase temperatures are equal. As the temperature of the two-phase mixture is increased to point E, on horizontal tie line DEF at 225°F, the mole fraction of H in the liquid phase decreases to  $x_H = 0.17$  (because it is more volatile than O and preferentially vaporizes), and the mole fraction of H in the vapor phase increases

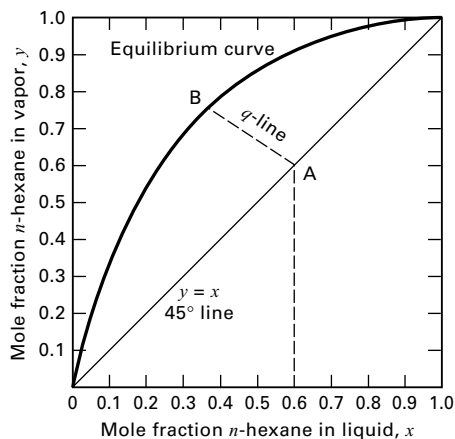


**Figure 4.3** Use of the  $T$ - $y$ - $x$  phase equilibrium diagram for the  $n$ -hexane- $n$ -octane system at 1 atm.

to  $y_H = 0.55$ . Throughout the two-phase region, the vapor is at its dew point, and the equilibrium liquid is at its bubble point. The overall composition of the two phases remains at a mole fraction of 0.30 for hexane. At point E, the relative phase amounts are determined by the inverse-lever-arm rule using the lengths of line segments DE and EF. Referring to Figures 4.1b and 4.3,  $V/L = DE/EF$  or  $V/F = DE/DEF$ . When the temperature is increased to 245°F, point G, the dew point for  $y_H = 0.3$ , is reached, where only a differential amount of liquid remains. An increase in temperature to point H at 275°F gives a superheated vapor with  $y_H = 0.30$ .

Constant-pressure  $x$ - $y$  plots like Figure 4.2b are useful because the vapor-and-liquid compositions are points on the equilibrium curve. However, temperatures are not included. Such plots include a 45° reference line,  $y = x$ . The  $y$ - $x$  plot of Figure 4.4 for H–O at 101.3 kPa is convenient for determining compositions as a function of mole-percent vaporization by geometric constructions as follows.

Consider feed mixture  $F$  in Figure 4.1b, of overall composition  $z_H = 0.6$ . To determine the phase compositions if, say, 60 mol% of the feed is vaporized, the dashed-line construction in Figure 4.4 is used. Point A on the 45° line represents  $z_H$ . Point B is reached by extending a line, called the  $q$ -line, upward and to the left toward the equilibrium curve at a slope equal to  $[(V/F) - 1]/(V/F)$ . Thus, for 60 mol% vaporization, the slope =  $(0.6 - 1)/0.6 = -\frac{2}{3}$ . Point B at the intersection of line AB with the equilibrium curve is the equilibrium composition  $y_H = 0.76$  and  $x_H = 0.37$ . This computation requires a trial-and-error placement of a horizontal line using



**Figure 4.4** Use of the  $y$ - $x$  phase-equilibrium diagram for the  $n$ -hexane- $n$ -octane system at 1 atm.

Figure 4.3. The derivation of the slope of the  $q$ -line in Figure 4.4 follows by combining

$$Fz_H = Vy_H + Lx_H$$

with the total mole balance,

$$F = V + L$$

to eliminate  $L$ , giving the  $q$ -line equation:

$$y_H = \left[ \frac{(V/F) - 1}{(V/F)} \right] x_H + \left[ \frac{1}{(V/F)} \right] z_H$$

Thus, the slope of the  $q$ -line passing through the equilibrium point  $(y_H, x_H)$  is  $[(V/F) - 1]/(V/F)$  and the line does pass through the point  $z_H = x_H = y_H$ .

Figure 4.2c is seldom used, but it illustrates, for a fixed temperature, the extent to which the mixture deviates from Raoult's law, which predicts the total pressure to be

$$\begin{aligned} P &= P_A^s x_A + P_B^s x_B \\ &= P_A^s x_A + P_B^s (1 - x_A) \\ &= P_B^s + x_A (P_A^s - P_B^s) \end{aligned} \quad (4-6)$$

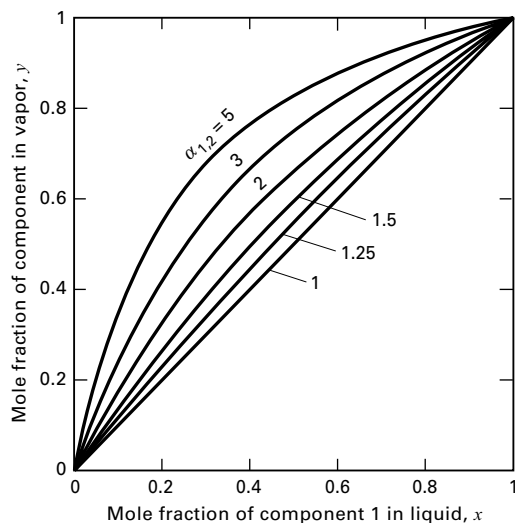
Thus, in this case, a plot of  $P$  versus  $x_A$  is a straight line with intersections at the vapor pressure of B for  $x_A = 0$  and that of A for  $x_B = 0$ . The greater the departure from a straight line, the greater the deviation from Raoult's law.

If the vapor phase is as in Figure 4.2c, deviations from Raoult's law are positive, and species liquid-phase activity coefficients are greater than 1; if the curve is concave, deviations are negative and activity coefficients are less than 1. In either case, the total pressure is

$$P = \gamma_A P_A^s x_A + \gamma_B P_B^s x_B \quad (4-7)$$

For narrow-boiling binary mixtures that exhibit ideal or nearly ideal behavior, the relative volatility,  $\alpha_{A,B}$ , varies little with pressure. If  $\alpha_{A,B}$  is constant over the entire composition range, the  $y$ - $x$  phase-equilibrium curve can be determined and plotted from a rearrangement of (4-5):

$$y_A = \frac{\alpha_{A,B} x_A}{1 + x_A (\alpha_{A,B} - 1)} \quad (4-8)$$



**Figure 4.5** Vapor-liquid equilibrium curves for constant values of relative volatility.

If Raoult's law applies,  $\alpha_{A,B}$  can be approximated by

$$\alpha_{A,B} = \frac{K_A}{K_B} = \frac{P_A^s/P}{P_B^s/P} = \frac{P_A^s}{P_B^s} \quad (4-9)$$

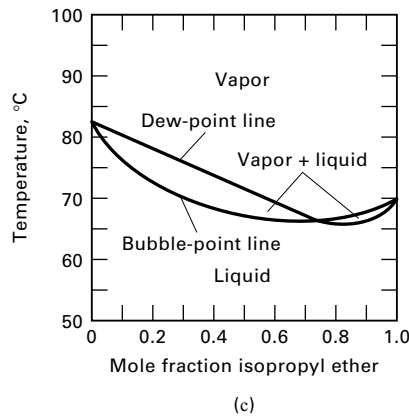
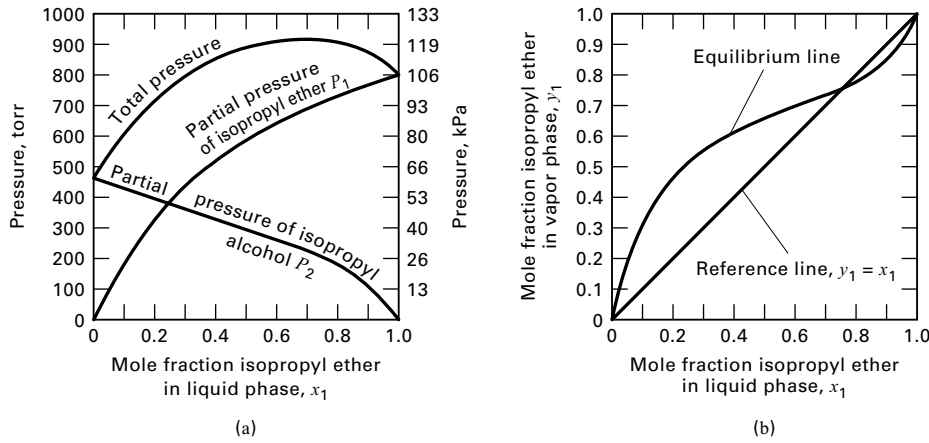
Thus, from a knowledge of just the vapor pressures of the two components at a given temperature, a  $y$ - $x$  phase-equilibrium curve can be approximated using only one value of  $\alpha_{A,B}$ . Families of curves, as shown in Figure 4.5, can be used for preliminary calculations in the absence of detailed experimental data. The use of (4-8) and (4-9) is not recommended for wide-boiling or nonideal mixtures.

### §4.3 BINARY AZEOTROPIC SYSTEMS

Departures from Raoult's law commonly manifest themselves in the formation of *azeotropes*; indeed, many close-boiling, nonideal mixtures form azeotropes, particularly those of different chemical types. Azeotropic-forming mixtures exhibit either maximum- or minimum-boiling points at some composition, corresponding, respectively, to negative and positive deviations from Raoult's law. Vapor and liquid compositions are identical for an azeotrope; thus, all  $K$ -values are 1,  $\alpha_{A,B} = 1$ , and no separation can take place.

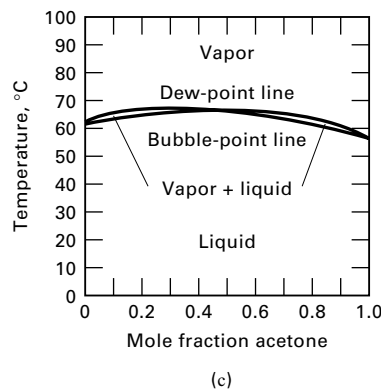
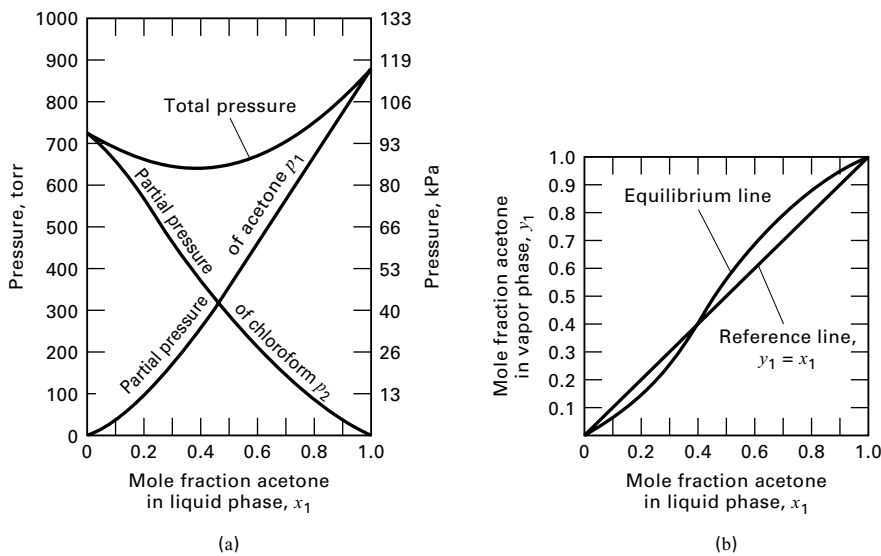
If only one liquid phase exists, it is a *homogeneous* azeotrope; if more than one liquid phase is present, the azeotrope is *heterogeneous*. By the Gibbs phase rule, at constant pressure in a two-component system, the vapor can coexist with no more than two liquid phases; in a ternary mixture, up to three liquid phases can coexist with the vapor, and so on,

Figures 4.6, 4.7, and 4.8 show three types of azeotropes. The most common by far is the minimum-boiling homogeneous azeotrope, e.g., isopropyl ether-isopropyl alcohol, shown in Figure 4.6. At a temperature of 70°C, the maximum total pressure is greater than the vapor pressure of either component, as shown in Figure 4.6a, because activity coefficients are greater than 1. The  $y$ - $x$  diagram in Figure 4.6b shows that for a pressure of 1 atm, the azeotropic mixture is at 78 mol% ether. Figure 4.6c is a  $T$ - $x$  diagram at 1 atm, where the

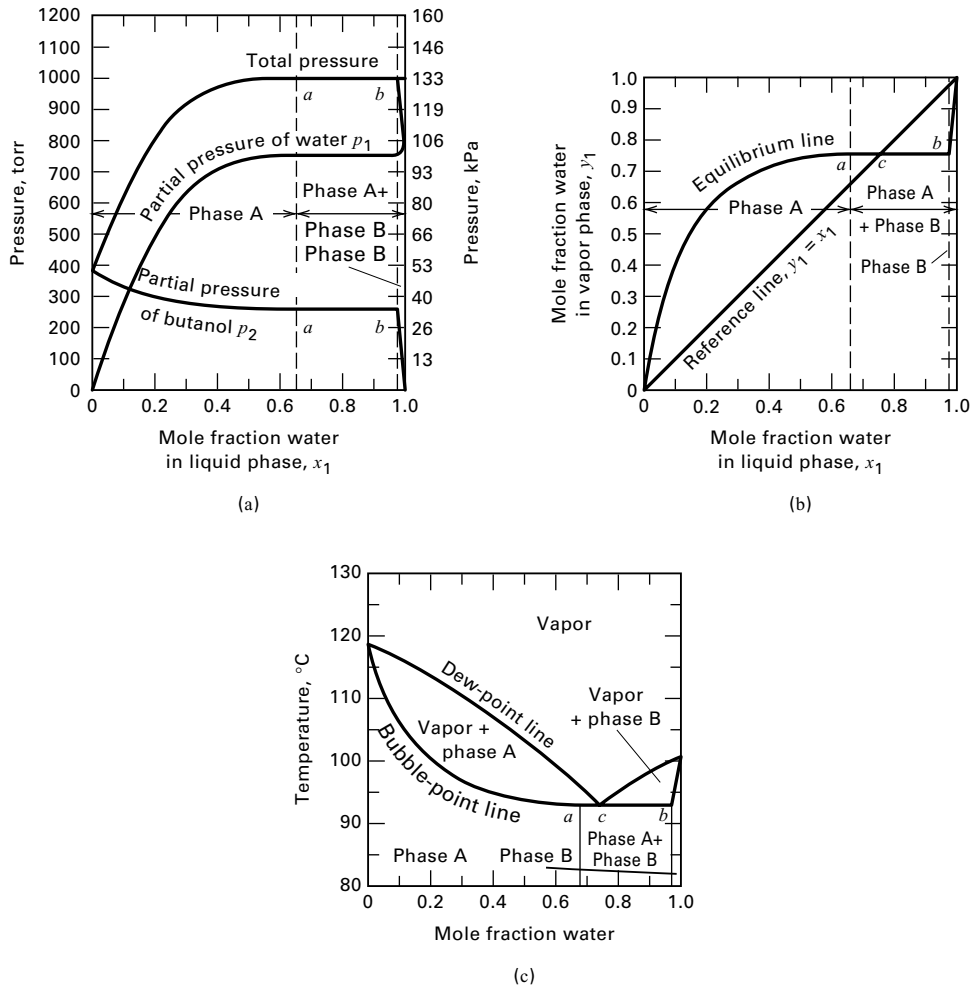


**Figure 4.6** Minimum-boiling-point azeotrope, isopropyl ether–isopropyl alcohol system: (a) partial and total pressures at 70°C; (b) vapor–liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa.

[Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part II*, 2nd ed., John Wiley & Sons, New York (1959).]



**Figure 4.7** Maximum-boiling-point azeotrope, acetone–chloroform system: (a) partial and total pressures at 60°C; (b) vapor–liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa pressure. [Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part II*, 2nd ed., John Wiley & Sons, New York (1959).]



**Figure 4.8** Minimum-boiling-point (two liquid phases) water/*n*-butanol system: (a) partial and total pressures at 100°C; (b) vapor–liquid equilibria at 101 kPa; (c) phase diagram at 101 kPa pressure.

[Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part II*, 2nd ed., John Wiley & Sons, New York (1959).]

azeotrope is seen to boil at 66°C. In Figure 4.6a, for 70°C, the azeotrope occurs at 123 kPa (923 torr), for 72 mol% ether. Thus, the azeotropic composition and temperature shift with pressure. In distillation, minimum-boiling azeotropic mixtures are approached in the overhead product.

For the maximum-boiling homogeneous azeotropic acetone–chloroform system in Figure 4.7a, the minimum total pressure at 60°C is below the vapor pressures of the pure components because activity coefficients are less than 1. The azeotrope is approached in the bottoms product in a distillation operation. Phase compositions at 1 atm are shown in Figures 4.7b and c.

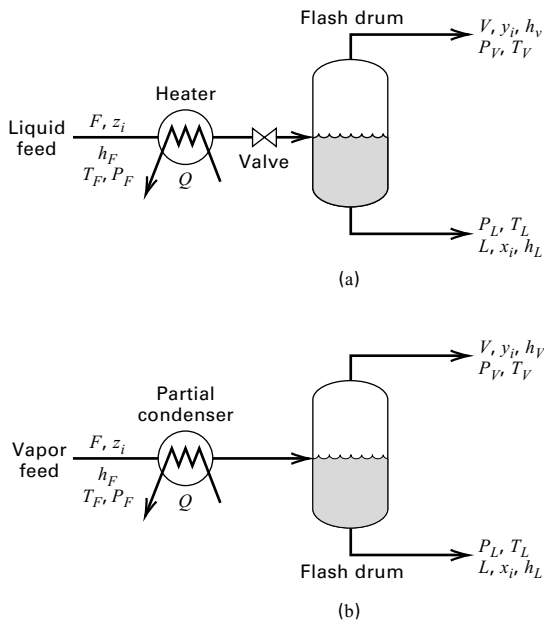
Heterogeneous azeotropes are minimum-boiling because activity coefficients must be significantly greater than 1 to form two liquid phases. The region a–b in Figure 4.8a for the water–*n*-butanol system is a two-phase region, where total and partial pressures remain constant as the amounts of the phases change, but phase compositions do not. The  $y$ – $x$  diagram in Figure 4.8b shows a horizontal line over the immiscible region, and the phase diagram of Figure 4.8c shows a minimum constant temperature.

To avoid azeotrope limitations, it is sometimes possible to shift the equilibrium by changing the pressure sufficiently to “break” the azeotrope, or move it away from the region where the required separation is to be made. For example, ethyl alcohol and water form a homogeneous minimum-boiling azeotrope of 95.6 wt% alcohol at 78.15°C and 101.3 kPa. However, at vacuums of less than 9.3 kPa, no azeotrope is formed. As discussed in Chapter 11, ternary azeotropes also occur, in which azeotrope formation in general, and heterogeneous azeotropes in particular, are employed to achieve difficult separations.

#### §4.4 MULTICOMPONENT FLASH, BUBBLE-POINT, AND DEW-POINT CALCULATIONS

A *flash* is a single-equilibrium-stage distillation in which a feed is partially vaporized to give a vapor richer than the feed in the more volatile components. In Figure 4.9a, (1) a pressurized liquid feed is heated and flashed adiabatically across a valve to a lower pressure, resulting in creation of a vapor phase that is separated from the remaining liquid in a flash





**Figure 4.9** Continuous, single-stage equilibrium separations: (a) flash vaporization and (b) partial condensation.

drum, or (2) if the valve is omitted, a liquid can be partially vaporized in a heater and then separated into two phases. Alternatively, a vapor feed can be cooled and partially condensed, as in Figure 4.9b, to give, after phase separation, a liquid richer in the less-volatile components. For properly designed systems, the streams leaving the drum will be in phase equilibrium [4].

Unless the relative volatility,  $\alpha_{AB}$ , is very large, flashing (partial vaporization) or partial condensation is not a replacement for distillation, but an auxiliary operation used to prepare streams for further processing.

Single-stage flash calculations are among the most common calculations in chemical engineering. They are used not only for the operations in Figure 4.9, but also to determine the phase condition of mixtures anywhere in a process, e.g. in a pipeline.

For the single-stage operation in Figure 4.9, the  $2C + 5$  equations listed in Table 4.3 apply. (In Figure 4.9,  $T$  and  $P$  are given separately for the vapor and liquid products to emphasize the need to assume mechanical and thermal equilibrium.) The equations relate the  $3C + 10$  variables ( $F, V, L, z_i, y_i, x_i, T_F, T_V, T_L, P_F, P_V, P_L, Q$ ) and leave  $C + 5$  degrees of freedom. Assuming that  $C + 3$  feed variables  $F, T_F, P_F$ , and  $C$  values of  $z_i$  are known, two additional variables can be specified for a flash calculation. The most common sets of specifications are:

|                |                            |
|----------------|----------------------------|
| $T_V, P_V$     | Isothermal flash           |
| $V/F = 0, P_L$ | Bubble-point temperature   |
| $V/F = 1, P_V$ | Dew-point temperature      |
| $T_L, V/F = 0$ | Bubble-point pressure      |
| $T_V, V/F = 1$ | Dew-point pressure         |
| $Q = 0, P_V$   | Adiabatic flash            |
| $Q, P_V$       | Nonadiabatic flash         |
| $V/F, P_V$     | Percent vaporization flash |

**Table 4.3** Equations for Single-Stage Flash Vaporization and Partial Condensation Operations. Feed mole fractions must sum to one.

| Equation  |                                     | Number of Equations    |
|---|-------------------------------------|------------------------|
| (1) $P_V = P_L$                                 | (mechanical equilibrium)            | 1                      |
| (2) $T_V = T_L$                                 | (thermal equilibrium)               | 1                      |
| (3) $y_i = K_i x_i$                             | (phase equilibrium)                 | $C$                    |
| (4) $Fz_i = Vy_i + Lx_i$                        | (component material balance)        | $C$                    |
| (5) $F = V + L$                                 | (total material balance)            | 1                      |
| (6) $h_F F + Q = h_V V + h_L L$                 | (energy balance)                    | 1                      |
| (7) $\sum_i y_i - \sum_i x_i = 0$               | (summations)                        | 1                      |
|   |                                     | $\mathcal{E} = 2C + 5$ |
| $K_i = K_i\{T_V, P_V, \mathbf{y}, \mathbf{x}\}$ | $h_F = h_F\{T_F, P_F, \mathbf{z}\}$ |                        |
| $h_V = h_V\{T_V, P_V, \mathbf{y}\}$             | $h_L = h_L\{T_L, P_L, \mathbf{x}\}$ |                        |

#### §4.4.1 Isothermal Flash

If the equilibrium temperature  $T_V$  (or  $T_L$ ) and the equilibrium pressure  $P_V$  (or  $P_L$ ) in the drum are specified, values of the remaining  $2C + 5$  variables are determined from  $2C + 5$  equations as given in Table 4.3.

*Isothermal-flash calculations* are not straightforward because Eq. (4) in Table 4.3 is a nonlinear equation in the unknowns  $V, L, y_i$ , and  $x_i$ . The solution procedure of Rachford and Rice [5], widely used in process simulators and described next, is given in Table 4.4.

Equations containing only a single unknown are solved first. Thus, Eqs. (1) and (2) in Table 4.3 are solved, respectively, for  $P_L$  and  $T_L$ . The unknown  $Q$  appears only in (6), so  $Q$  is computed after all other equations have been solved. This leaves Eqs. (3), (4), (5), and (7) in Table 4.3 to be solved for  $V, L$ , and all values of  $y$  and  $x$ . These equations can be partitioned to solve for the unknowns in a sequential manner

**Table 4.4** Rachford–Rice Procedure for Isothermal-Flash Calculations When  $K$ -Values Are Independent of Composition

Specified variables:  $F, T_F, P_F, z_1, z_2, \dots, z_C, T_V, P_V$

##### Steps

- (1)  $T_L = T_V$
- (2)  $P_L = P_V$
- (3) Solve

$$f\{\Psi\} = \sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)} = 0$$

for  $\Psi = V/F$ , where  $K_i = K_i\{T_V, P_V\}$ .

- (4)  $V = F\Psi$
- (5)  $x_i = \frac{z_i}{1 + \Psi(K_i - 1)}$
- (6)  $y_i = \frac{z_i K_i}{1 + \Psi(K_i - 1)} = x_i K_i$
- (7)  $L = F - V$
- (8)  $Q = h_V V + h_L L - h_F F$

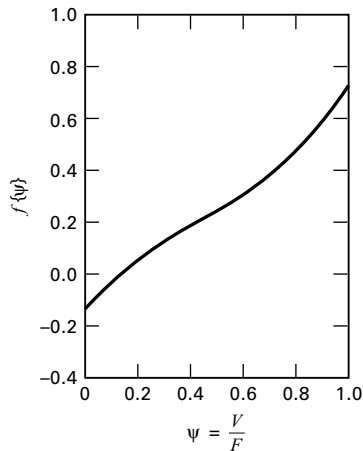


Figure 4.10 Rachford–Rice function for Example 4.1.

by substituting Eq. (5) into Eq. (4) to eliminate  $L$  and combining the result with Eq. (3) to obtain Eqs. (5) and (6) in Table 4.4. Here (5) is in  $x_i$  but not  $y_i$ , and (6) is in  $y_i$  but not  $x_i$ . Summing these two equations and combining them with  $\sum y_i - \sum x_i = 0$  to eliminate  $y_i$  and  $x_i$  gives Eq. (3) in Table 4.4, a nonlinear equation in  $V$  (or  $\Psi = V/F$ ) only. Upon solving this equation numerically in an iterative manner for  $\Psi$  and then  $V$ , from Eq. (4), the remaining unknowns are obtained directly from Eqs. (5) through (8) in Table 4.4. When  $T_F$  and/or  $P_F$  are not specified, Eq. (6) of Table 4.3 is not solved for  $Q$ .

Equation (3) of Table 4.4 can be solved iteratively by guessing values of  $\Psi$  between 0 and 1 until the function  $f\{\Psi\} = 0$ . A typical function, encountered in Example 4.1, is shown in Figure 4.10. The most widely employed procedure for solving Eq. (3) of Table 4.4 is Newton's method [6]. A value of the  $\Psi$  root for iteration  $k + 1$  is computed by the recursive relation

$$\Psi^{(k+1)} = \Psi^{(k)} - \frac{f\{\Psi^{(k)}\}}{f'\{\Psi^{(k)}\}} \quad (4-10)$$

where the superscript is the iteration index, and the derivative of  $f\{\Psi\}$ , from Eq. (3) in Table 4.4, with respect to  $\Psi$  is

$$f'\{\Psi^{(k)}\} = \sum_{i=1}^C \frac{z_i(1 - K_i)^2}{[1 + \Psi^{(k)}(K_i - 1)]^2} \quad (4-11)$$

The iteration can be initiated by assuming  $\Psi^{(1)} = 0.5$ . Sufficient accuracy is achieved by terminating the iterations when  $|\Psi^{(k+1)} - \Psi^{(k)}|/\Psi^{(k)} < 0.0001$ .

The existence of a valid root ( $0 \leq \Psi \leq 1$ ) must be checked before employing the procedure of Table 4.4, by checking if the equilibrium condition corresponds to subcooled liquid or superheated vapor rather than partial vaporization or condensation. A first estimate of whether a multicomponent feed gives a two-phase mixture is made by inspecting the  $K$ -values. If all  $K$ -values are  $> 1$ , the phase is superheated vapor. If all  $K$ -values are  $< 1$ , the single phase is a subcooled liquid. If one or more  $K$ -values are greater than 1 and one or more  $K$ -values are less than 1, the check is made by first

computing  $f\{\Psi\}$  from Eq. (3) in Table 4.4 for  $\Psi = 0$ . If the resulting  $f\{0\} > 0$ , the mixture is below its bubble point (subcooled liquid). Alternatively, if  $f\{1\} < 0$ , the mixture is above the dew point (superheated vapor). The Rachford–Rice procedure may fail to converge if  $K$ -values are sensitive to composition. In that case, the method of Boston and Britt [19] is employed in some process simulators.

#### EXAMPLE 4.1 Phase Conditions of a Process Stream.

A 100-kmol/h feed consisting of 10, 20, 30, and 40 mol% of propane (3),  $n$ -butane (4),  $n$ -pentane (5), and  $n$ -hexane (6), respectively, enters a distillation column at 100 psia (689.5 kPa) and 200°F (366.5°K). Assuming equilibrium, what fraction of the feed enters as liquid, and what are the liquid and vapor compositions?

#### Solution

At flash conditions, from Figure 2.4,  $K_3 = 4.2$ ,  $K_4 = 1.75$ ,  $K_5 = 0.74$ ,  $K_6 = 0.34$ , independent of compositions. Because some  $K$ -values are greater than 1 and some less than 1, it is necessary first to compute values of  $f\{0\}$  and  $f\{1\}$  for Eq. (3) in Table 4.4 to see if the mixture is between the bubble and dew points.

$$f\{0\} = \frac{0.1(1 - 4.2)}{1} + \frac{0.2(1 - 1.75)}{1} + \frac{0.3(1 - 0.74)}{1} + \frac{0.4(1 - 0.34)}{1} = -0.128$$

Since  $f\{0\}$  is not more than zero, the mixture is above the bubble point. Now compute  $f\{1\}$ :

$$f\{1\} = \frac{0.1(1 - 4.2)}{1 + (4.2 - 1)} + \frac{0.2(1 - 1.75)}{1 + (1.75 - 1)} + \frac{0.3(1 - 0.74)}{1 + (0.74 - 1)} + \frac{0.4(1 - 0.34)}{1 + (0.34 - 1)} = 0.720$$

Since  $f\{1\}$  is not less than zero, the mixture is below the dew point. Therefore, the mixture is part vapor. Using the Rachford–Rice procedure and substituting  $z_i$  and  $K_i$  values into Eq. (3) of Table 4.4 gives

$$0 = \frac{0.1(1 - 4.2)}{1 + \Psi(4.2 - 1)} + \frac{0.2(1 - 1.75)}{1 + \Psi(1.75 - 1)} + \frac{0.3(1 - 0.74)}{1 + \Psi(0.74 - 1)} + \frac{0.4(1 - 0.34)}{1 + \Psi(0.34 - 1)}$$

Solving this equation by Newton's method using an initial guess for  $\Psi$  of 0.50 gives the following iteration history:

| $k$ | $\Psi^{(k)}$ | $f\{\Psi^{(k)}\}$ | $f'\{\Psi^{(k)}\}$ | $\Psi^{(k+1)}$ | $\left  \frac{\Psi^{(k+1)} - \Psi^{(k)}}{\Psi^{(k)}} \right $ |
|-----|--------------|-------------------|--------------------|----------------|---|
| 1   | 0.5000       | 0.2515            | 0.6259             | 0.0982         | 0.8037  |
| 2   | 0.0982       | -0.0209           | 0.9111             | 0.1211         | 0.2335  |
| 3   | 0.1211       | -0.0007           | 0.8539             | 0.1219         | 0.0065  |
| 4   | 0.1219       | 0.0000            | 0.8521             | 0.1219         | 0.0000  |

Convergence is rapid, giving  $\Psi = V/F = 0.1219$ . From Eq. (4) of Table 4.4, the vapor flow rate is  $0.1219(100) = 12.19$  kmol/h, and the liquid flow rate from Eq. (7) is  $(100 - 12.19) = 87.81$  kmol/h. Liquid and vapor compositions from Eqs. (5) and (6) are

|                   | $x$           | $y$           |
|-------------------|---------------|---------------|
| Propane           | 0.0719        | 0.3021        |
| <i>n</i> -Butane  | 0.1833        | 0.3207        |
| <i>n</i> -Pentane | 0.3098        | 0.2293        |
| <i>n</i> -Hexane  | <u>0.4350</u> | <u>0.1479</u> |
| Sum               | 1.0000        | 1.0000        |

A plot of  $f\{\Psi\}$  as a function of  $\Psi$  is shown in Figure 4.10.

### §4.4.2 Bubble and Dew Points

At the *bubble point*,  $\Psi = 0$  and  $f\{0\} = 0$ . By Eq. (3) of Table 4.4

$$f\{0\} = \sum_i z_i(1 - K_i) = \sum z_i - \sum z_i K_i = 0$$

However,  $\sum z_i = 1$ . Therefore, the bubble-point equation is

$$\boxed{\sum_i z_i K_i = 1} \quad (4-12)$$

At the *dew point*,  $\Psi = 1$  and  $f\{1\} = 0$ . From Eq. (3) of Table 4.4,

$$f\{1\} = \sum_i \frac{z_i(1 - K_i)}{K_i} = \sum \frac{z_i}{K_i} - \sum z_i = 0$$

Therefore, the dew-point equation is

$$\boxed{\sum_i \frac{z_i}{K_i} = 1} \quad (4-13)$$

For a given feed composition,  $z_i$ , (4-12) or (4-13) can be used to find  $T$  for a specified  $P$  or to find  $P$  for a specified  $T$ .

The bubble- and dew-point equations are nonlinear in temperature, but only moderately nonlinear in pressure, except in the region of the *convergence pressure*, where  $K$ -values of very light or very heavy species change drastically with pressure, as in Figure 2.6. Therefore, iterative procedures are required to solve for bubble- and dew-point conditions except if Raoult's law  $K$ -values are applicable. Substitution of  $K_i = P_i^s/P$  into (4-12) allows direct calculation of bubble-point pressure:

$$P_{\text{bubble}} = \sum_{i=1}^C z_i P_i^s \quad (4-14)$$

where  $P_i^s$  is the temperature-dependent vapor pressure of species  $i$ . Similarly, from (4-13), the dew-point pressure is

$$P_{\text{dew}} = \left( \sum_{i=1}^C \frac{z_i}{P_i^s} \right)^{-1} \quad (4-15)$$

Another exception occurs for mixtures at the bubble point when  $K$ -values can be expressed by the modified Raoult's law,  $K_i = \gamma_i P_i^s/P$ . Substituting into (4-12)

$$P_{\text{bubble}} = \sum_{i=1}^C \gamma_i z_i P_i^s \quad (4-16)$$

Thus, liquid activity coefficients can be computed at a known bubble-point temperature and composition, since  $x_i = z_i$  at the bubble point.

Bubble- and dew-point calculations are used to determine saturation conditions for liquid and vapor streams. Whenever there is vapor-liquid equilibrium, the vapor is at its dew point and the liquid is at its bubble point.

#### EXAMPLE 4.2 Bubble-Point Temperature.

In Figure 1.9, the  $nC_4$ -rich bottoms product from Column C3 has the composition given in Table 1.5. If the pressure at the bottom of the distillation column is 100 psia (689 kPa), estimate the mixture temperature.

#### Solution

The bottoms product is a liquid at its bubble point with the following composition:

| Component         | kmol/h       | $z_i = x_i$   |
|-------------------|--------------|---------------|
| <i>i</i> -Butane  | 8.60         | 0.0319        |
| <i>n</i> -Butane  | 215.80       | 0.7992        |
| <i>i</i> -Pentane | 28.10        | 0.1041        |
| <i>n</i> -Pentane | <u>17.50</u> | <u>0.0648</u> |
|                   | 270.00       | 1.0000        |

The bubble-point temperature can be estimated by finding the temperature that will satisfy (4-12), using  $K$ -values from Figure 2.4. Because the bottoms product is rich in  $nC_4$ , assume the  $K$ -value of  $nC_4$  is 1. From Figure 2.4, for 100 psia,  $T = 150^\circ\text{F}$ . For this temperature, using Figure 2.4 to obtain  $K$ -values of the other three components and substituting these values and the  $z$ -values into (4-12),

$$\begin{aligned} \sum z_i K_i &= 0.0319(1.3) + 0.7992(1.0) + 0.1041(0.47) \\ &\quad + 0.0648(0.38) \\ &= 0.042 + 0.799 + 0.049 + 0.025 = 0.915 \end{aligned}$$

The sum is not 1.0, so another temperature is assumed and the summation repeated. To increase the sum, the  $K$ -values must increase and, thus, the temperature must increase as well. Because the sum is dominated by  $nC_4$ , assume its  $K$ -value = 1.09. This corresponds to a temperature of  $160^\circ\text{F}$ , which results in a summation of 1.01. By linear interpolation,  $T = 159^\circ\text{F}$ .

#### EXAMPLE 4.3 Bubble-Point Pressure.

Cyclopentane is separated from cyclohexane by liquid-liquid extraction with methanol at  $25^\circ\text{C}$ . To prevent vaporization, the mixture must be above the bubble-point pressure. Calculate that pressure using the following compositions, activity coefficients, and vapor pressures:

|                         | Methanol | Cyclohexane | Cyclopentane |
|-------------------------|----------|-------------|--------------|
| Vapor pressure, psia    | 2.45     | 1.89        | 6.14         |
| Methanol-rich layer:    |          |             |              |
| $x$                     | 0.7615   | 0.1499      | 0.0886       |
| $\gamma$                | 1.118    | 4.773       | 3.467        |
| Cyclohexane-rich layer: |          |             |              |
| $x$                     | 0.1737   | 0.5402      | 0.2861       |
| $\gamma$                | 4.901    | 1.324       | 1.074        |

**Solution**

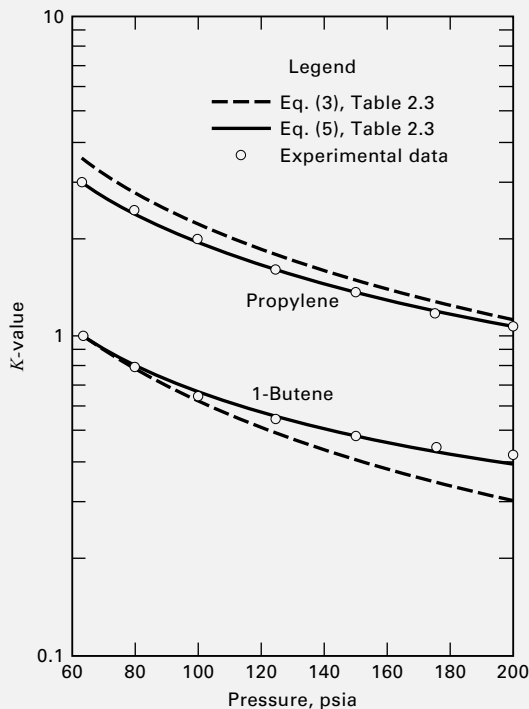
Assume the modified Raoult's law in the form of (4-16) applies for either liquid phase. If the methanol-rich-layer data are used:

$$\begin{aligned} P_{\text{bubble}} &= 1.118(0.7615)(2.45) + 4.773(0.1499)(1.89) \\ &\quad + 3.467(0.0886)(6.14) \\ &= 5.32 \text{ psia (36.7 kPa)} \end{aligned}$$

A similar calculation based on the cyclohexane-rich layer gives an identical result because the data are consistent; thus  $\gamma_{iL}^{(1)} x_i^{(1)} = \gamma_{iL}^{(2)} x_i^{(2)}$ . A pressure higher than 5.32 psia will prevent formation of vapor at this location in the extraction process. Operation at atmospheric pressure is viable.

**EXAMPLE 4.4 Distillation column operating pressure.**

Propylene (P) is separated from 1-butene (B) by distillation into a vapor distillate containing 90 mol% propylene. Calculate the column pressure if the partial condenser exit temperature is 100°F (37.8°C), the lowest attainable temperature with cooling water. Determine the composition of the liquid reflux. In Figure 4.11,  $K$ -values estimated from Eq. (5) of Table 2.3, using the Redlich-Kwong equation of state for vapor fugacity, are plotted and compared to experimental data [7] and Raoult's law  $K$ -values.



**Figure 4.11**  $K$ -values for propylene/1-butene system at 100°F.

**Solution**

The column pressure is at the dew point for the vapor distillate. The reflux composition is that of a liquid in equilibrium with the vapor distillate at its dew point. The method of false position [8] is used to perform the calculations by rewriting (4-13) in the form

$$f\{P\} = \sum_{i=1}^C \frac{z_i}{K_i} - 1 \quad (1)$$

The recursion relationship for the method of false position is based on the assumption that  $f\{P\}$  is linear in  $P$  such that

$$P^{(k+2)} = P^{(k+1)} - f\{P^{(k+1)}\} \left[ \frac{P^{(k+1)} - P^{(k)}}{f\{P^{(k+1)}\} - f\{P^{(k)}\}} \right] \quad (2)$$

This is reasonable because, at low pressures,  $K$ -values in (2) are almost inversely proportional to pressure. Two values of  $P$  are required to initialize this formula. Choose 100 psia and 190 psia. At  $P^{(1)} = 100$  psia,  $K$ -values from the solid lines in Figure 4.11, when substituted into Eq. (1) give,

$$f\{P\} = \frac{0.90}{2.0} + \frac{0.10}{0.68} - 1.0 = -0.40$$

Similarly, for  $P^{(2)} = 190$  psia,  $f\{P\} = +0.02$ . Substitution into Eq. (2) gives  $P^{(3)} = 186$ , and so on. Iterations end when  $|P^{(k+2)} - P^{(k+1)}|/P^{(k+1)} < 0.005$ . In this example, that occurs when  $k = 3$ . Thus, the operating pressure at the partial condenser outlet is 186 psia (1,282 kPa). The liquid reflux composition is obtained from  $x_i = z_i/K_i$ , using  $K$ -values at that pressure. The final results are:

| Component | Equilibrium Mole Fraction |               |
|-----------|---------------------------|---------------|
|           | Vapor Distillate          | Liquid Reflux |
| Propylene | 0.90                      | 0.76          |
| 1-Butene  | 0.10                      | 0.24          |
|           | 1.00                      | 1.00          |

**§4.4.3 Adiabatic Flash**

When the pressure of a liquid stream is reduced adiabatically across a valve as in Figure 4.9a, an *adiabatic-flash* ( $Q = 0$ ) calculation is made to determine the resulting phases, temperature, compositions, and flow rates for a specified downstream pressure. The calculation is made by applying the isothermal-flash calculation procedure of §4.4.1 in an iterative manner. First a guess is made of the flash temperature,  $T_V$ . Then  $\Psi$ ,  $V$ ,  $x$ ,  $y$ , and  $L$  are determined, as for an isothermal flash, from steps 3 through 7 in Table 4.4. The guessed value of  $T_V$  (equal to  $T_L$ ) is next checked by an energy balance obtained by combining Eqs. (7) and (8) of Table 4.4 with  $Q = 0$  to give

$$f\{T_V\} = \frac{\Psi h_V + (1 - \Psi)h_L - h_F}{1,000} = 0 \quad (4-17)$$

where division by 1,000 makes the terms of the order 1. Enthalpies are computed at  $T_V = T_L$ . If the computed value of  $f\{T_V\}$  is not zero, the entire procedure is repeated. A plot of  $f\{T_V\}$  versus  $T_V$  is interpolated to determine the correct value of  $T_V$ . The procedure is tedious because it involves inner-loop iteration on  $\Psi$  and outer-loop iteration on  $T_V$ .

Outer-loop iteration on  $T_V$  is successful when Eq. (3) of Table 4.4 is not sensitive to the guess of  $T_V$ . This is the case for wide-boiling mixtures. For close-boiling mixtures, the algorithm may fail because of sensitivity to the value of  $T_V$ . In this case, it is preferable to do the outer-loop iteration on  $\Psi$  and solve Eq. (3) of Table 4.4 for  $T_V$  in the inner loop, using a

guessed value for  $\Psi$  to initiate the process, as follows:

$$f\{T_V\} = \sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)} = 0 \quad (4-18)$$

Then, Eqs. (5) and (6) of Table 4.4 are solved for  $x$  and  $y$ . Equation (4-17) is then solved directly for  $\Psi$ , since

$$f\{\Psi\} = \frac{\Psi h_V + (1 - \Psi)h_L - h_F}{1,000} = 0 \quad (4-19)$$

from which

$$\Psi = \frac{h_F - h_L}{h_V - h_L} \quad (4-20)$$

If  $\Psi$  from (4-20) is not equal to the guessed  $\Psi$ , a new  $\Psi$  is used to repeat the outer loop, starting with (4-18).

Multicomponent, isothermal-flash, bubble-point, dew-point, and adiabatic-flash calculations are tedious. Especially for nonideal mixtures, required thermodynamic property expressions are complex, and calculations should be made with a process simulator.

#### EXAMPLE 4.5 Adiabatic Flash of the Feed to a Distillation Column.

Equilibrium liquid from the flash drum at 120°F and 485 psia in Example 2.6 is fed to a so-called “*stabilizer*” distillation tower to remove the remaining hydrogen and methane. Feed-plate pressure of the stabilizer is 165 psia (1,138 kPa). Calculate the percent molar vaporization of the feed and compositions of the vapor and liquid if the pressure is decreased adiabatically from 485 to 165 psia by a valve and pipeline pressure drop.

#### Solution

This problem, involving a wide-boiling feed, is best solved by using a process simulator. Using the CHEMCAD program with  $K$ -values and enthalpies from the P–R equation of state (Table 2.5), the result is:

| Component      | kmol/h                 |                         |                          |
|----------------|------------------------|-------------------------|--------------------------|
|                | Feed 120°F<br>485 psia | Vapor 112°F<br>165 psia | Liquid 112°F<br>165 psia |
| Hydrogen       | 1.0                    | 0.7                     | 0.3                      |
| Methane        | 27.9                   | 15.2                    | 12.7                     |
| Benzene        | 345.1                  | 0.4                     | 344.7                    |
| Toluene        | 113.4                  | 0.04                    | 113.36                   |
| Total          | 487.4                  | 16.34                   | 471.06                   |
| Enthalpy, kJ/h | −1,089,000             | 362,000                 | −1,451,000               |

The results show that only a small amount of vapor ( $\Psi = 0.0035$ ), predominantly  $H_2$  and  $CH_4$ , is produced. The flash temperature of 112°F is 8°F below the feed temperature. The enthalpy of the feed is equal to the sum of the vapor and liquid product enthalpies for this adiabatic operation.

## §4.5 TERNARY LIQUID–LIQUID SYSTEMS

Ternary mixtures that undergo phase splitting to form two separate liquid phases differ as to the extent of solubility of

the three components in the two liquid phases. The simplest case is in Figure 4.12a, where only the *solute*, component B, has any appreciable solubility in either the *carrier*, A, or the *solvent*, C, both of which have negligible (although never zero) solubility in each other. Here, equations can be derived for a single equilibrium stage, using the variables  $F$ ,  $S$ ,  $E$ , and  $R$  to refer, respectively, to the flow rates (or amounts) of the feed, solvent, exiting extract (C-rich), and exiting raffinate (A-rich). By definition, the extract is the exiting liquid phase that contains the extracted solute; the raffinate is the exiting liquid phase that contains the portion of the solute, B, that is not extracted. By convention, the extract is shown as leaving from the top of the stage even though it may not have the smaller density. If the entering solvent contains no B, it is convenient to write material-balance and phase-equilibrium equations for the solute, B, in terms of molar or mass flow rates. Often, it is preferable to express compositions as mass or mole ratios instead of fractions, as follows:

Let:  $F_A$  = feed rate of carrier A;  $S$  = flow rate of solvent C;  $X_B$  = ratio of *mass* (or moles) of solute B, to mass (or moles) of the other component in the feed (F), raffinate(R), or extract (E).

Then, the solute material balance is

$$X_B^{(F)} F_A = X_B^{(E)} S + X_B^{(R)} F_A \quad (4-21)$$

and the distribution of solute at equilibrium is given by

$$X_B^{(E)} = K'_{D_B} X_B^{(R)} \quad (4-22)$$

where  $K'_{D_B}$  is the distribution or partition coefficient in terms of mass or mole ratios (instead of mass or mole fractions). Substituting (4-22) into (4-21) to eliminate  $X_B^{(E)}$ ,

$$X_B^{(R)} = \frac{X_B^{(F)} F_A}{F_A + K'_{D_B} S} \quad (4-23)$$

A useful parameter is the *extraction factor*,  $E_B$ , for the solute B:

$$E_B = K'_{D_B} S / F_A \quad (4-24)$$

Large extraction factors result from large distribution coefficients or large ratios of solvent to carrier. Substituting (4-24) into (4-23) gives the fraction of B not extracted as

$$\boxed{X_B^{(R)} / X_B^{(F)} = \frac{1}{1 + E_B}} \quad (4-25)$$

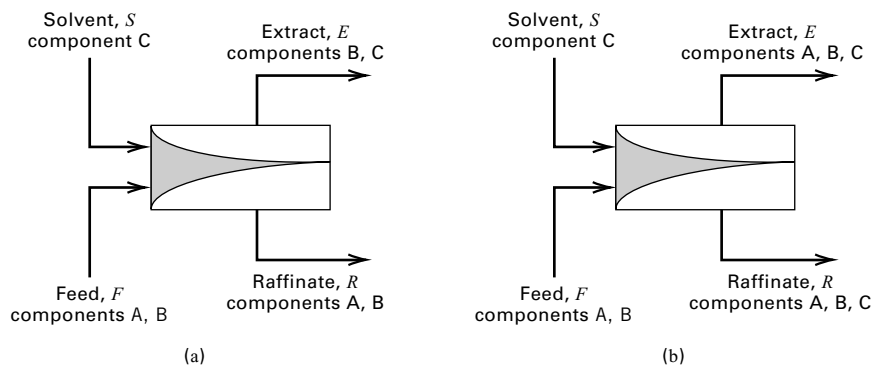
Thus, the larger the extraction factor, the smaller the fraction of B not extracted *or* the larger the fraction of B extracted. Alternatively, the fraction of B extracted is 1 minus (4-25) or  $E_B / (1 + E_B)$ .

Mass (mole) ratios,  $X$ , are related to mass (mole) fractions,  $x$ , by

$$X_i = x_i / (1 - x_i) \quad (4-26)$$

Values of the distribution coefficient,  $K'_D$ , in terms of ratios, are related to  $K_D$  in terms of fractions as given in (2-20) by

$$K'_{D_i} = \frac{x_i^{(1)} / (1 - x_i^{(1)})}{x_i^{(2)} / (1 - x_i^{(2)})} = K_{D_i} \left( \frac{1 - x_i^{(2)}}{1 - x_i^{(1)}} \right) \quad (4-27)$$



**Figure 4.12** Phase splitting of ternary mixtures: (a) components A and C mutually insoluble; (b) components A and C partially soluble.

where (1) and (2) are the equilibrium solvent-rich and solvent-poor liquid phases, respectively. When values of  $x_i$  are small,  $K'_D$  approaches  $K_D$ . As discussed in Chapter 2, the distribution (partition) coefficient, which can be determined from activity coefficients by  $K_{D_B} = \gamma_B^{(2)}/\gamma_B^{(1)}$  when mole fractions are used, varies with compositions and temperature. When the raffinate and extract are both dilute, solute activity coefficients can be approximated by values at infinite dilution so that  $K_{D_B}$  can be taken as constant at a given temperature. An extensive listing of such  $K_{D_B}$  values for various ternary systems is given in *Perry's Chemical Engineers' Handbook* [9]. If values for  $F_B$ ,  $X_B^{(F)}$ ,  $S$ , and  $K_{D_B}$  are given, (4-25) can be solved for  $X_B^{(R)}$ .

#### EXAMPLE 4.6 Single-Stage Extraction of Acetic Acid.

Methyl isobutyl ketone (C) is used as a solvent to remove acetic acid (B) from a 13,500 kg/h feed of 8 wt% acid in water (A), because distillation would require vaporization of large amounts of water. If the raffinate is to contain 1 wt% acetic acid, estimate the kg/h of solvent for a single equilibrium stage.

#### Solution

Assume the water and solvent are immiscible. From *Perry's Chemical Engineers' Handbook*,  $K_D = 0.657$  in mass-fraction units. For the low concentrations of acetic acid, assume  $K'_D = K_D$ .

$$F_A = (0.92)(13,500) = 12,420 \text{ kg/h}$$

$$X_B^{(F)} = (13,500 - 12,420)/12,420 = 0.087$$

The raffinate is to contain 1 wt% B. Therefore,

$$X_B^{(R)} = 0.01/(1 - 0.01) = 0.0101$$

From (4-25), solving for  $E_B$ ,

$$E_B = \frac{X_B^{(F)}}{X_B^{(R)}} - 1 = (0.087/0.0101) - 1 = 7.61$$

From (4-24), the definition of the extraction factor,

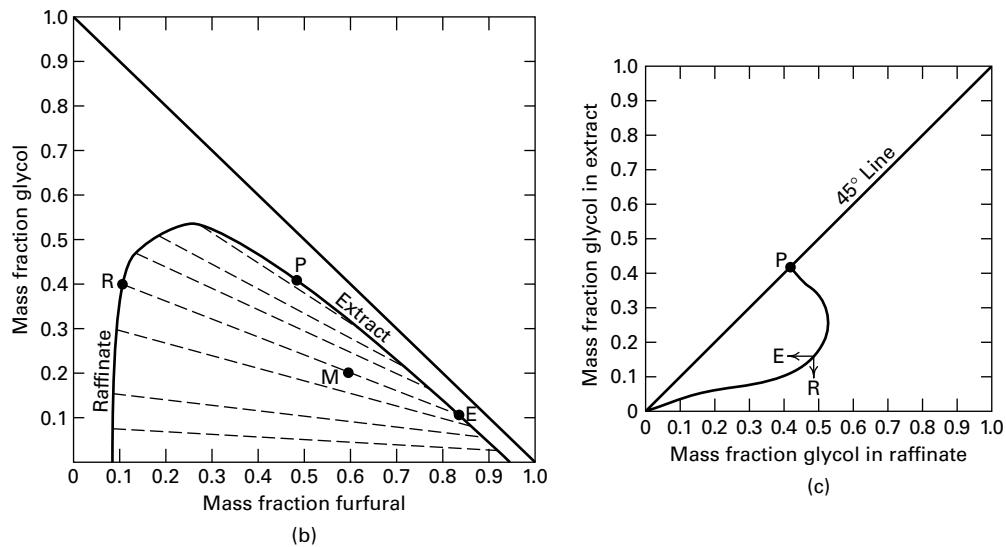
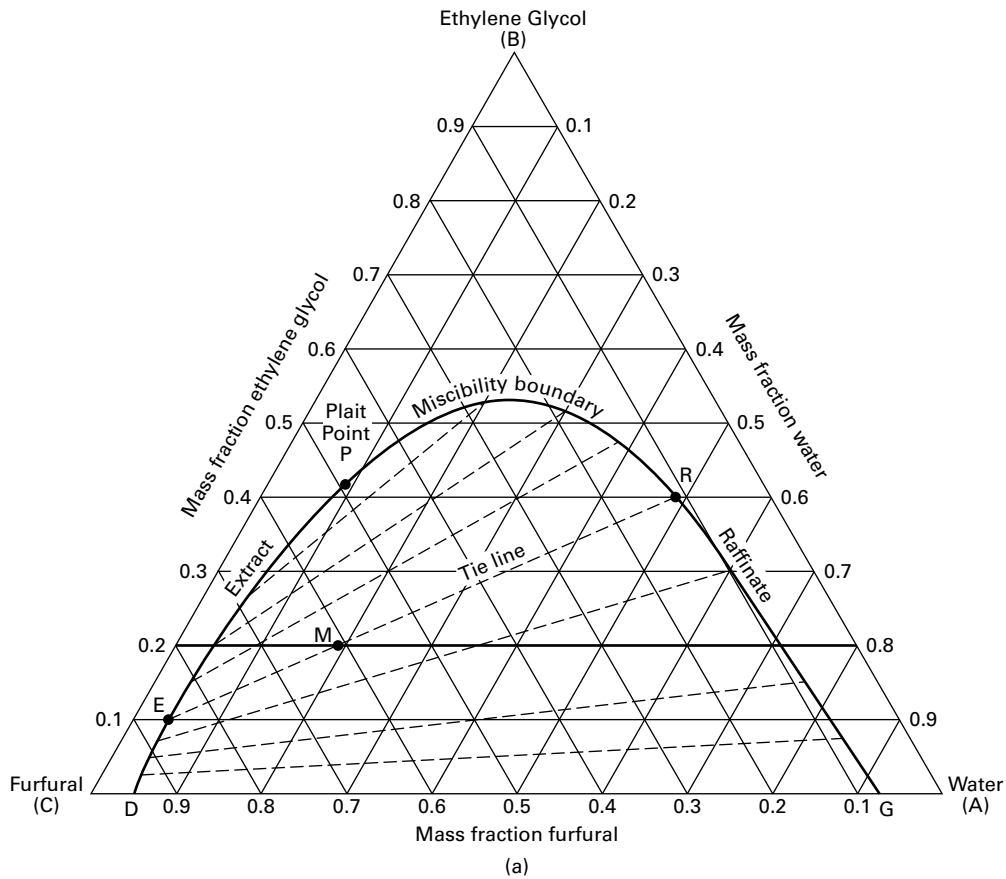
$$S = \frac{E_B F_A}{K'_D} = 7.61(12,420/0.657) = 144,000 \text{ kg/h}$$

This solvent/feed flow-rate ratio is very large. The use of multiple stages, as discussed in Chapter 5, could reduce the solvent rate, or a solvent with a larger distribution coefficient could be sought. For example, 1-butanol as the solvent, with  $K_D = 1.613$ , would halve the solvent flow.

In the ternary liquid–liquid system shown in Figure 4.12b, components A and C are partially soluble in each other, and component B distributes between the extract and raffinate phases. This case is the most commonly encountered, and different phase diagrams and computational techniques have been devised for making calculations of equilibrium compositions and phase amounts. Examples of ternary-phase diagrams are shown in Figure 4.13 for the ternary system water (A)–ethylene glycol (B)–furfural (C) at 25°C and a pressure of 101 kPa, which is above the bubble-point pressure. Experimental data are from Conway and Norton [18]. Water–ethylene glycol and furfural–ethylene glycol are completely miscible pairs, while furfural–water is a partially miscible pair. Furfural can be used as a solvent to remove the solute, ethylene glycol, from water, where the furfural-rich phase is the extract, and the water-rich phase is the raffinate.

Figure 4.13a, an equilateral-triangular diagram, is the most common form of display of ternary liquid–liquid equilibrium data. Each apex is a pure component of the mixture. Each edge is a mixture of the two pure components at the terminal apexes of the side. Any point located within the triangle is a ternary mixture. In such a diagram the sum of the lengths of three perpendicular lines drawn from any interior point to the edges equals the altitude of the triangle. Thus, if each of these three lines is scaled from 0 to 100, the percent of, say, furfural, at any point such as M, is simply the length of the line perpendicular to the edge opposite the pure furfural apex. The determination of the composition of an interior point is facilitated by the three sets of parallel lines on the diagram, where each set is in mass-fraction increments of 0.1 (or 10%), and is parallel to an edge of the triangle opposite the apex of the component, whose mass fraction is given. Thus, the point M in Figure 4.13a represents a mixture of feed and solvent (before phase separation) containing 19 wt% water, 20 wt% ethylene glycol, and 61 wt% furfural.

Miscibility limits for the furfural–water binary system are at D and G. The miscibility boundary (saturation or binodal curve) DEPRG for the system is obtained experimentally by a *cloud-point titration*. For example, water is added to a completely miscible (and clear) 50 wt% solution of furfural and glycol, and it is noted that the onset of cloudiness, due to formation of a second phase, occurs when the mixture is 11% water, 44.5% furfural, and 44.5% glycol by weight. Other



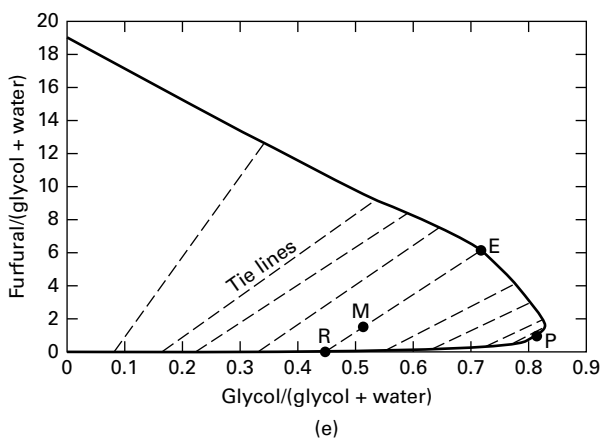
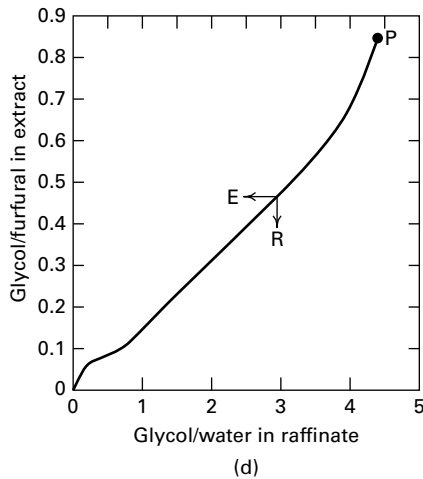
**Figure 4.13** Liquid–liquid equilibrium, ethylene glycol–furfural–water, 25°C, 101 kPa: (a) equilateral-triangular diagram; (b) right-triangular diagram; (c) equilibrium solute diagram in mass fractions; (*continues*)

miscibility data are given in Table 4.5, from which the miscibility curve in Figure 4.13a was drawn.

Tie lines, shown as dashed lines below the miscibility boundary, connect equilibrium-phase composition points on the miscibility boundary. To obtain data to construct tie line ER, it is necessary to make a mixture such as M (20% glycol, 19% water, 61% furfural), equilibrate it, and then chemically analyze the resulting equilibrium extract and raffinate phases

E and R (in this case, 10% glycol, 4% water, and 86% furfural; and 40% glycol, 49% water, and 11% furfural, respectively). At point P, the *plait point*, the two liquid phases have identical compositions. Therefore, the tie lines converge to point P and the two phases become one phase. Tie-line data for this system are listed in Table 4.6, in terms of glycol composition.

When there is mutual phase solubility, thermodynamic variables necessary to define the equilibrium system are  $T$ ,  $P$ ,



**Figure 4.13** (continued) (d) equilibrium solute diagram in mass ratios; (e) Janecke diagram.

**Table 4.5** Equilibrium Miscibility Data in Weight Percent for the Furfural–Ethylene Glycol–Water System at 25°C and 101 kPa

| Furfural | Ethylene Glycol | Water |
|----------|-----------------|-------|
| 95.0     | 0.0             | 5.0   |
| 90.3     | 5.2             | 4.5   |
| 86.1     | 10.0            | 3.9   |
| 75.1     | 20.0            | 4.9   |
| 66.7     | 27.5            | 5.8   |
| 49.0     | 41.5            | 9.5   |
| 34.3     | 50.5            | 15.2  |
| 27.5     | 52.5            | 20.0  |
| 13.9     | 47.5            | 38.6  |
| 11.0     | 40.0            | 49.0  |
| 9.7      | 30.0            | 60.3  |
| 8.4      | 15.0            | 76.6  |
| 7.7      | 0.0             | 92.3  |

**Table 4.6** Mutual Equilibrium (Tie-Line) Data for the Furfural–Ethylene Glycol–Water System at 25°C and 101 kPa

| Glycol in Water Layer, wt% | Glycol in Furfural Layer, wt% |
|----------------------------|-------------------------------|
| 41.5                       | 41.5                          |
| 50.5                       | 32.5                          |
| 52.5                       | 27.5                          |
| 51.5                       | 20.0                          |
| 47.5                       | 15.0                          |
| 40.0                       | 10.0                          |
| 30.0                       | 7.5                           |
| 20.0                       | 6.2                           |
| 15.0                       | 5.2                           |
| 7.3                        | 2.5                           |

and component concentrations in each phase. According to the phase rule, (4-1), for a three-component, two-liquid-phase system, there are three degrees of freedom. With  $T$  and  $P$  specified, the concentration of one component in either phase suffices to completely define the equilibrium system. As shown in Figure 4.13a, one value for percent glycol on the miscibility boundary curve fixes the composition and, by means of the tie line, the composition of the other phase.

Figure 4.13b represents the same system on a right-triangular diagram. Here, concentrations in wt% of any two components (normally the solute and solvent) are given. Concentration of the third is obtained by the difference from 100 wt%. Diagrams like this are easier to construct and read than equilateral-triangular diagrams. However, equilateral-triangular diagrams are conveniently constructed with CSpace, which can be downloaded from the web site [www.ugr.es/~cspace/Whatis.htm](http://www.ugr.es/~cspace/Whatis.htm).

Figures 4.13c and 4.13d represent the same ternary system in terms of weight fraction and weight ratios of solute, respectively. Figure 4.13c is simply a plot of equilibrium (tie-line) data of Table 4.6 in terms of solute mass fraction. In Figure 4.13d, mass ratios of solute (ethylene glycol) to furfural and water for the extract and raffinate phases, respectively, are used. Such curves can be used to interpolate tie lines, since only a limited number of tie lines are shown on triangular graphs. Because of this, such diagrams are often referred to as *distribution diagrams*. When mole (rather than mass) fractions are used in a diagram like Figure 4.13c, a nearly straight line is often evident near the origin, whose slope is the distribution coefficient  $K_D$  for the solute at infinite dilution.

In 1906, Janecke [10] suggested the data display shown as Figure 4.13e. Here, the mass of solvent per unit mass of solvent-free liquid, furfural/(water + glycol), is plotted as the ordinate versus mass ratio, on a solvent-free basis, of glycol/(water + glycol) as the abscissa. The ordinate and abscissa apply to both phases. Equilibrium conditions are connected by tie lines. Mole ratios can also be used to construct Janecke diagrams.

Any of the diagrams in Figure 4.13 can be used for solving problems involving material balances subject to liquid–liquid equilibrium constraints.



**EXAMPLE 4.7 Single-Equilibrium Stage Extraction Using Diagrams.**

Determine extract and raffinate compositions when a 45 wt% glycol (B)–55 wt% water (A) solution is contacted with twice its weight of pure furfural solvent (C) at 25°C and 101 kPa. Use each of the five diagrams in Figure 4.13, if possible.

**Solution**

Assume a basis of 100 g of 45% glycol–water feed. Thus, in Figure 4.12b, the feed ( $F$ ) is 55 g A and 45 g B. The solvent ( $S$ ) is 200 g C. Let  $E$  denote the extract, and  $R$  the raffinate.

(a) Using the equilateral-triangular diagram of Figure 4.14:

**Step 1.** Locate the feed and solvent compositions at points  $F$  and  $S$ , respectively.

**Step 2.** Define mixing point  $M$  as  $M = F + S = E + R$ .

**Step 3.** Apply the inverse-lever-arm rule. Let  $w_i^{(1)}$  be the mass fraction of species  $i$  in the extract,  $w_i^{(2)}$  be the fraction of species  $i$  in the raffinate, and  $w_i^{(M)}$  be the fraction of species  $i$  in the feed-plus-solvent phases.

From a solvent balance, C:  $(F + S)w_C^{(M)} = Fw_C^{(F)} + Sw_C^{(S)}$ .

$$\frac{F}{S} = \frac{w_C^{(S)} - w_C^{(M)}}{w_C^{(M)} - w_C^{(F)}} \quad (1)$$

Thus, points  $S$ ,  $M$ , and  $F$  lie on a straight line, as they should, and, by the inverse-lever-arm rule,

$$\frac{F}{S} = \frac{SM}{MF} = \frac{1}{2}$$

The composition at point  $M$  is 18.3% A, 15.0% B, and 66.7% C.

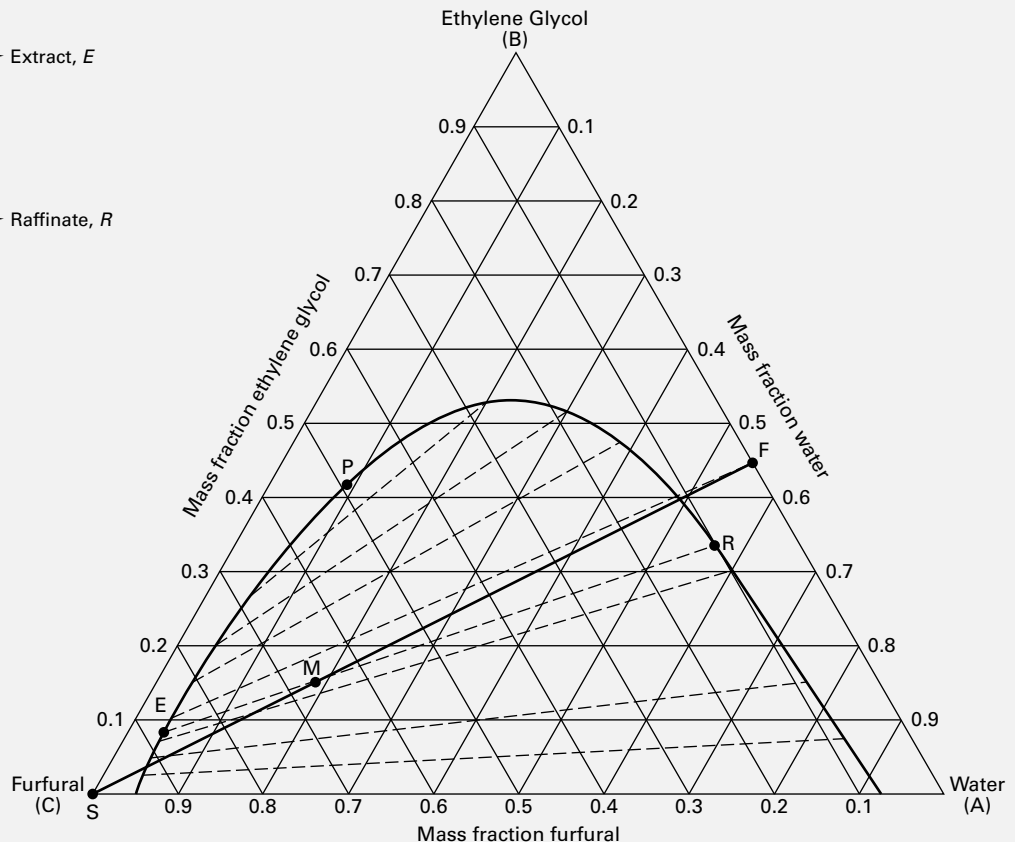
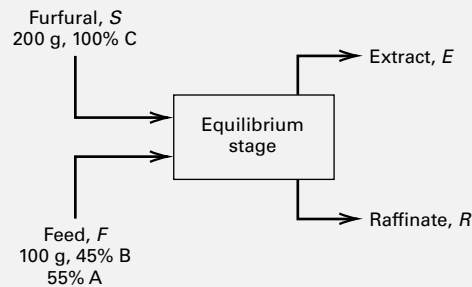


Figure 4.14 Solution to Example 4.7a.

**Step 4.** Since  $M$  lies in the two-phase region, the mixture must separate along an interpolated dash-dot tie line into an extract phase at point  $E$  (8.5% B, 4.5% A, and 87.0% C) and the raffinate at point  $R$  (34.0% B, 56.0% A, and 10.0% C).

**Step 5.** The inverse-lever-arm rule applies to points  $E$ ,  $M$ , and  $R$ , so  $E = M(\overline{RM}/\overline{ER})$ .  $M = 100 + 200 = 300$  g. From measurements of line segments,  $E = 300(147/200) = 220$  g and  $R = M - E = 300 - 220 = 80$  g.

(b) Using the right-triangular diagram of Figure 4.15:

**Step 1.** Locate the  $F$  and  $S$  for the two feed streams.

**Step 2.** Define the mixing point  $M = F + S$ .

**Step 3.** The inverse-lever-arm rule also applies to right-triangular diagrams, so  $MF/MS = \frac{1}{2}$ .

**Step 4.** Points  $R$  and  $E$  are on the ends of the interpolated dash-dot tie line passing through point  $M$ .

The numerical results of part (b) are identical to those of part (a).

(c) By the equilibrium solute diagram of Figure 4.13c, a material balance on glycol B,

$$Fw_B^{(F)} + Sw_B^{(S)} = 45 = Ew_B^{(E)} + Rw_B^{(R)} \quad (2)$$

must be solved simultaneously with a phase-equilibrium relationship. It is not possible to do this graphically using Figure 4.13c in any straightforward manner unless the solvent (C) and carrier (A) are mutually insoluble. The outlet-stream composition can be found, however, by the following iterative procedure.

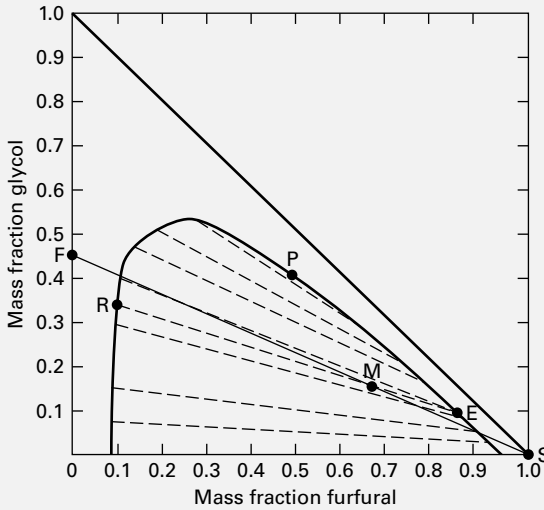


Figure 4.15 Solution to Example 4.7b.

**Step 1.** Guess a value for  $w_B^{(E)}$  and read the equilibrium value,  $w_B^{(R)}$ , from Figure 4.13c.

**Step 2.** Substitute these two values into the equation obtained by combining (2) with the overall balance,  $E + R = 300$ , to eliminate  $R$ . Solve for  $E$  and then  $R$ .

**Step 3.** Check to see if the furfural (or water) balance is satisfied using the data from Figures 4.13a, 4.13b, or 4.13c. If not, repeat steps 1 to 3 with a new guess for  $w_B^{(E)}$ . This procedure leads to the results obtained in parts (a) and (b).

(d) Figure 4.13d, a mass-fraction plot, suffers from the same limitations as Figure 4.13c. A solution must again be achieved by an iterative procedure.

(e) With the Janecke diagram of Figure 4.16:

**Step 1.** The feed mixture is located at point F. With the addition of 200 g of pure furfural solvent,  $M = F + S$  is located as shown, since the ratio of glycol to (glycol + water) remains the same.

**Step 2.** The mixture at point M separates into the two phases at points E and R using the interpolated dash-dot tie line, with the coordinates (7.1, 0.67) at E and (0.10, 0.37) at R.

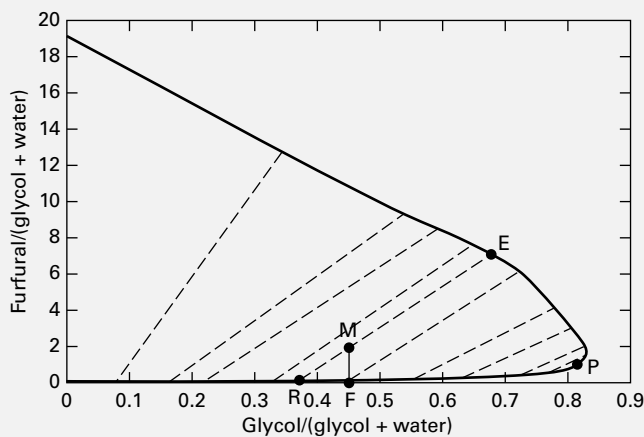


Figure 4.16 Solution to Example 4.7e.

**Step 3.** Let  $Z^E$  and  $Z^R$  equal the total mass of components A and B in the extract and raffinate, respectively. Then, the following balances apply:

$$\begin{aligned} \text{Furfural: } 7.1Z^E + 0.10Z^R &= 200 \\ \text{Glycol: } 0.67Z^E + 0.37Z^R &= 45 \end{aligned}$$

Solving these equations,  $Z^E = 27$  g and  $Z^R = 73$  g.

Thus, the furfural in the extract =  $(7.1)(27)$  = 192 g, the furfural in the raffinate =  $200 - 192 = 8$  g, the glycol in the extract =  $(0.67)(27)$  = 18 g, the glycol in the raffinate =  $45 - 18 = 27$  g, the water in the raffinate =  $73 - 27 = 46$  g, and the water in the extract =  $27 - 18 = 9$  g. Total extract is  $192 + 27 = 219$  g, which is close to the results of part (a). The raffinate composition and amount can be obtained just as readily.

It should be noted on the Janecke diagram that  $\overline{ME}/\overline{MR}$  does not equal  $R/E$ ; it equals  $R/E$  on a solvent-free basis.

In Figure 4.13, two pairs of components are mutually soluble, while one pair is only partially soluble. Ternary systems where two pairs and even all three pairs are only partially soluble also exist. Figure 4.17 shows examples, from Francis [11] and Findlay [12], of four cases where two pairs of components are only partially soluble.

In Figure 4.17a, two two-phase regions are formed, while in Figure 4.17c, in addition to the two-phase regions, a three-phase region, RST, exists. In Figure 4.17b, the two separate two-phase regions merge. For a ternary mixture, as temperature is reduced, phase behavior may progress from Figure 4.17a to 4.17b to 4.17c. In Figures 4.17a, 4.17b, and 4.17c, all tie lines slope in the same direction. In some systems *solventropy*, a reversal of tie-line slopes, occurs.

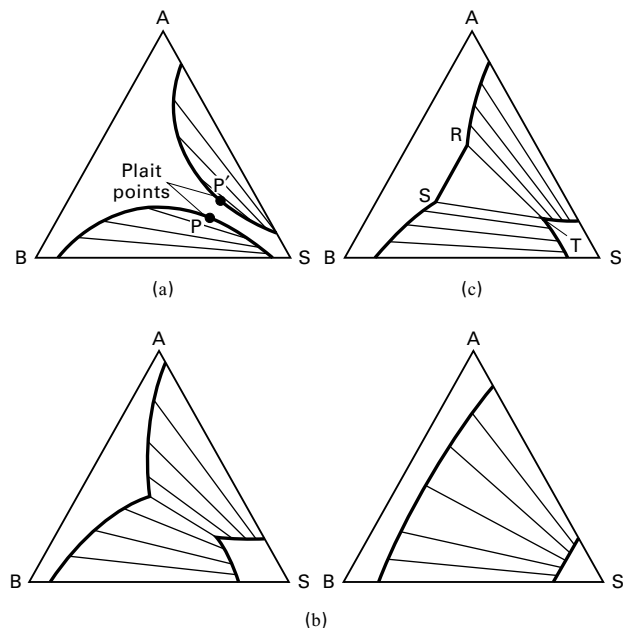


Figure 4.17 Equilibria for 3/2 systems: (a) miscibility boundaries are separate; (b) miscibility boundaries and tie-line equilibria merge; (c) tie lines do not merge and the three-phase region RST is formed.

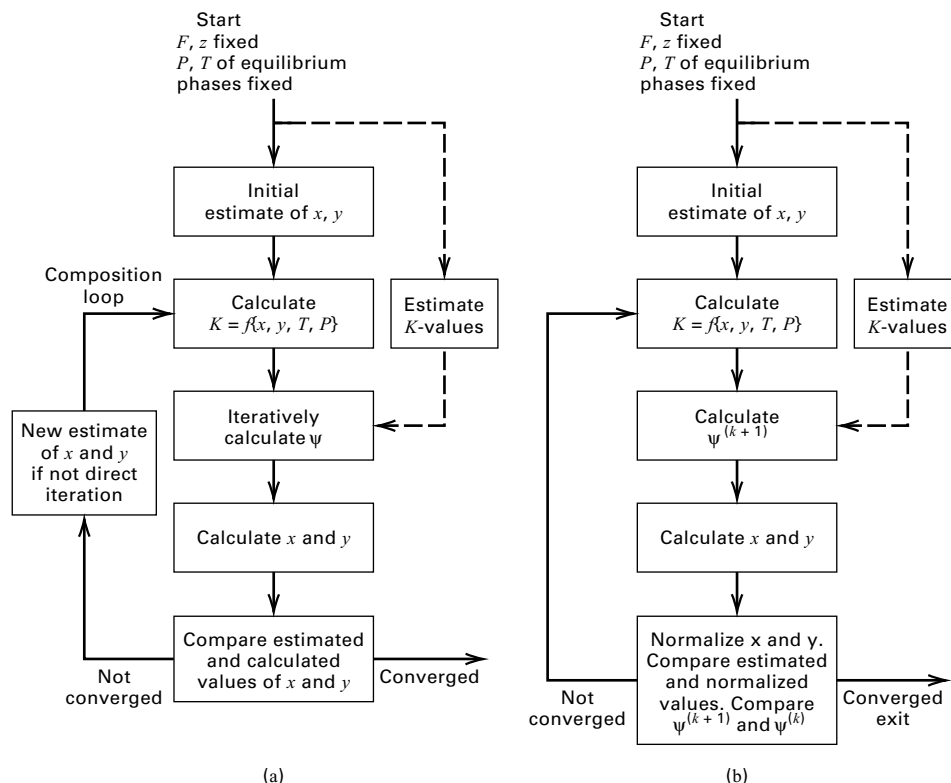
### §4.6 MULTICOMPONENT LIQUID–LIQUID SYSTEMS

Quarternary and higher multicomponent mixtures are encountered in extraction processes, particularly when two solvents are used. Multicomponent liquid–liquid equilibria are complex, and there is no compact, graphical way of representing phase–equilibria data. Accordingly, the computation of equilibrium–phase compositions is best made by process simulators using activity–coefficient equations that account for the effect of composition (e.g., NRTL, UNIQUAC, or UNIFAC). One such method is a modification of the Rachford–Rice algorithm for vapor–liquid equilibrium from Tables 4.3 and 4.4. For extraction, symbol transformations are made and moles are used instead of mass.

| Vapor–Liquid Equilibria      | Liquid–Liquid Equilibria               |
|------------------------------|--|
| Feed, $F$                    | Feed, $F$ , + solvent, $S$             |
| Equilibrium vapor, $V$       | Extract, $E$ ( $L^{(1)}$ )             |
| Equilibrium liquid, $L$      | Raffinate, $R$ ( $L^{(2)}$ )           |
| Feed mole fractions, $z_i$   | Mole fractions of combined $F$ and $S$ |
| Vapor mole fractions, $y_i$  | Extract mole fractions, $x_i^{(1)}$    |
| Liquid mole fractions, $x_i$ | Raffinate mole fractions, $x_i^{(2)}$  |
| $K$ -value, $K_i$            | Distribution coefficient, $K_{D,i}$    |
| $\Psi = V/F$                 | $\Psi = E/F$                           |

Industrial extraction processes are commonly adiabatic so, if the feeds are at identical temperatures, the only energy effect is the heat of mixing, which is usually sufficiently small that isothermal assumptions are justified.

The modified Rachford–Rice algorithm is shown in Figure 4.18. This algorithm is applicable for an isothermal vapor–liquid or liquid–liquid stage calculation when  $K$ -values depend strongly on phase compositions. The algorithm requires that feed and solvent flow rates and compositions be fixed, and that pressure and temperature be specified. An initial estimate is made of the phase compositions,  $x_i^{(1)}$  and  $x_i^{(2)}$ , and corresponding estimates of the distribution coefficients are made from liquid-phase activity coefficients using (2-30) with, for example, the NRTL or UNIQUAC equations discussed in Chapter 2. Equation (3) of Table 4.4 is then solved iteratively for  $\Psi = E/(F + S)$ , from which values of  $x_i^{(2)}$  and  $x_i^{(1)}$  are computed from Eqs. (5) and (6), respectively, of Table 4.4. Resulting values of  $x_i^{(1)}$  and  $x_i^{(2)}$  will not usually sum to 1 for each phase and are therefore normalized using equations of the form  $x'_i = x_i/\sum x_j$ , where  $x'_i$  are the normalized values that force  $\sum x'_j$  to equal 1. Normalized values replace the values computed from Eqs. (5) and (6). The iterative procedure is repeated until the compositions  $x_i^{(1)}$  and  $x_i^{(2)}$  no longer change by more than three or four significant digits from one iteration to the next. Multicomponent liquid–liquid equilibrium calculations are best carried out with a process simulator.



**Figure 4.18** Algorithm for isothermal-flash calculation when  $K$ -values are composition-dependent: (a) separate nested iterations on  $\Psi$  and  $(x, y)$ ; (b) simultaneous iteration on  $\Psi$  and  $(x, y)$ .

**EXAMPLE 4.8 Liquid-Liquid Equilibrium for a Four-Component Mixture.**

An azeotropic mixture of isopropanol, acetone, and water is dehydrated with ethyl acetate in a system of two distillation columns. Benzene was previously used as the dehydrating agent, but legislation has made benzene undesirable because it is carcinogenic. Ethyl acetate is far less toxic. The overhead vapor from the first column, with the composition below, at 20 psia and 80°C, is condensed and cooled to 35°C, without significant pressure drop, causing the formation of two liquid phases assumed to be in equilibrium. Estimate the amounts of the phases in kg/h and the equilibrium phase compositions in wt%.

| Component     | kg/h   |
|---------------|--------|
| Isopropanol   | 4,250  |
| Acetone       | 850    |
| Water         | 2,300  |
| Ethyl acetate | 43,700 |

Note that the specification of this problem conforms with the degrees of freedom predicted by (4-4), which for  $C = 4$  is 9.

**Solution**

This example was solved with the CHEMCAD program using the UNIFAC method to estimate liquid-phase activity coefficients. The results are:

| Component       | Weight Fraction    |                  |
|-----------------|--------------------|------------------|
|                 | Organic-Rich Phase | Water-Rich Phase |
| Isopropanol     | 0.0843             | 0.0615           |
| Acetone         | 0.0169             | 0.0115           |
| Water           | 0.0019             | 0.8888           |
| Ethyl acetate   | <u>0.8969</u>      | <u>0.0382</u>    |
|                 | 1.0000             | 1.0000           |
| Flow rate, kg/h | 48,617             | 2,483            |

It is of interest to compare the distribution coefficients from the UNIFAC method to values given in *Perry's Handbook* [1]:

| Component     | Distribution Coefficient (wt% Basis) |                         |
|---------------|--------------------------------------|-------------------------|
|               | UNIFAC                               | <i>Perry's Handbook</i> |
| Isopropanol   | 1.37                                 | 1.205 (20°C)            |
| Acetone       | 1.47                                 | 1.50 (30°C)             |
| Water         | 0.0021                               | —                       |
| Ethyl acetate | 23.5                                 | —                       |

Results for isopropanol and acetone are in agreement at these dilute conditions, considering the temperature differences.

**§4.7 SOLID-LIQUID SYSTEMS**

Solid-liquid separations include leaching, crystallization, and adsorption. In leaching (solid-liquid extraction), a multi-component solid mixture is separated by contacting the solid with a solvent that selectively dissolves some of the solid species. Although this operation is quite similar to liquid-liquid extraction, leaching is a much more difficult operation in practice in that diffusion in solids is very slow compared to diffusion in liquids, thus making it difficult to achieve equilibrium. Also, it is impossible to completely separate a solid phase from a liquid phase. A solids-free liquid phase can be obtained, but the solids will always be accompanied by some liquid. In comparison, complete separation of two liquid phases is fairly easy to achieve.

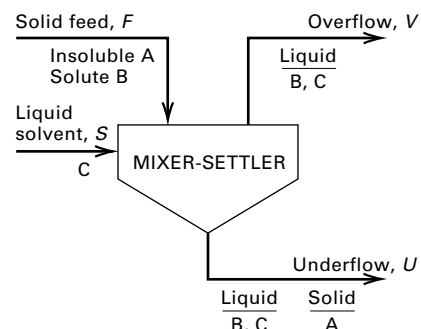
Crystallization or precipitation of a component from a liquid mixture is an operation in which equilibrium can be achieved, but a sharp phase separation is again impossible. A drying step is always needed because crystals occlude liquid.

A third application of solid-liquid systems, adsorption, involves use of a porous solid agent that does not undergo phase or composition change. Instead, it selectively adsorbs liquid species, on its exterior and interior surfaces. Adsorbed species are then desorbed and the solid adsorbing agent is regenerated for repeated use. Variations of adsorption include ion exchange and chromatography. A solid-liquid system is also utilized in membrane-separation operations, where the solid is a membrane that selectively absorbs and transports selected species.

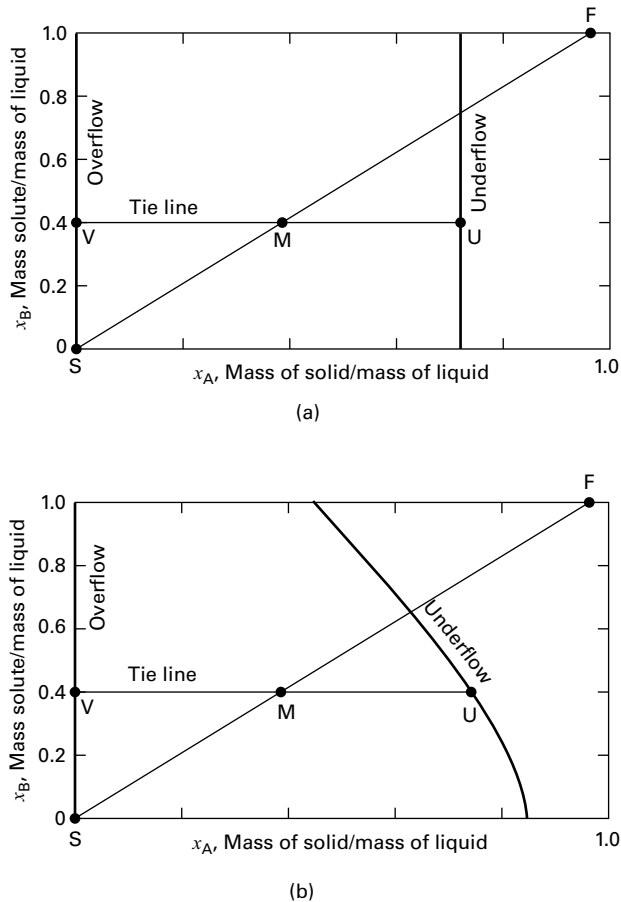
Solid-liquid separation processes, such as leaching and crystallization, almost always involve phase-separation operations such as gravity sedimentation, filtration, and centrifugation.

**§4.7.1 Leaching**

In Figure 4.19, the solid feed consists of particles of components A and B. The solvent, C, selectively dissolves B. Overflow from the stage is a solids-free solvent C and dissolved B. The underflow is a slurry of liquid and solid A. In an *ideal leaching stage*, all of the solute is dissolved by the solvent, whereas A is not dissolved. Also, the composition of the retained liquid phase in the underflow slurry is identical to the composition of the liquid overflow, and that overflow is free of solids. The mass ratio of solid to liquid in the underflow depends on the properties of the phases and the type of



**Figure 4.19** Leaching stage.



**Figure 4.20** Underflow–overflow conditions for ideal leaching: (a) constant-solution underflow; (b) variable-solution underflow.

equipment, and is best determined from experience or tests with prototype equipment. In general, if the viscosity of the liquid phases increases with increasing solute concentration, the mass ratio of solid to liquid in the underflow decreases because the solid retains more liquid.

Ideal leaching calculations can be done algebraically or with diagrams like Figure 4.20. Let:

- $F$  = total mass flow rate of feed to be leached
- $S$  = total mass flow rate of entering solvent
- $U$  = total mass flow rate of the underflow, including solids
- $V$  = total mass flow rate of the overflow
- $X_A$  = mass ratio of insoluble solid A to (solute B + solvent C) in the feed flow,  $F$ , or underflow,  $U$
- $Y_A$  = mass ratio of insoluble solid A to (solute B + solvent C) in the entering solvent flow,  $S$ , or overflow,  $V$
- $X_B$  = mass ratio of solute B to (solute B + solvent C) in the feed flow,  $F$ , or underflow,  $U$
- $Y_B$  = mass ratio of solute B to (solute B + solvent C) in the solvent flow,  $S$ , or overflow,  $V$

Figure 4.20a depicts ideal leaching conditions where, in the underflow, the mass ratio of insoluble solid to liquid,  $X_A$ , is a constant, independent of the concentration,  $X_B$ , of solute in the solids-free liquid. The resulting tie line is vertical. This is

*constant-solution underflow*. Figure 4.20b depicts ideal leaching conditions when  $X_A$  varies with  $X_B$ . This is *variable-solution underflow*. In both cases, the assumptions are: (1) an entering feed,  $F$ , free of solvent such that  $X_B = 1$ ; (2) a solids-free and solute-free solvent,  $S$ , such that  $Y_A = 0$  and  $Y_B = 0$ ; and (3) equilibrium between exiting liquid solutions in underflow,  $U$ , and overflow,  $V$ , such that  $X_B = Y_B$ ; and (4) a solids-free overflow,  $V$ , such that  $Y_A = 0$ .

A mixing point,  $M$ , can be defined for  $(F + S)$ , equal to that for the sum of the products of the leaching stage,  $(U + V)$ . Typical mixing points, and inlet and outlet compositions, are included in Figures 4.20a and b. In both cases, as shown in the next example, the inverse-lever-arm rule can be applied to line  $UMV$  to obtain flow rates of  $U$  and  $V$ .

#### EXAMPLE 4.9 Leaching of Soybeans to Recover Oil.

Soybeans are a predominant oilseed crop, followed by cottonseed, peanuts, and sunflower seed. While soybeans are not consumed directly by humans, they can be processed to produce valuable products. Production of soybeans in the United States began after World War II, increasing in recent years to more than 140 billion lb/yr. Most soybeans are converted to soy oil and vitamins like niacin and lecithin for humans, and defatted meal for livestock. Compared to other vegetable oils, soy oil is more economical and healthier. Typically, 100 pounds of soybeans yields 18 lb of soy oil and 79 lb of defatted meal.

To recover their oil, soybeans are first cleaned, cracked to loosen the seeds from the hulls, dehulled, and dried to 10–11% moisture. Before leaching, the soybeans are flaked to increase the mass-transfer rate of the oil out of the bean. They are leached with hexane to recover the oil. Following leaching, the hexane overflow is separated from the soy oil and recovered for recycle by evaporation, while the underflow is treated to remove residual hexane, and toasted with hot air to produce defatted meal. Modern soybean extraction plants crush up to 3,000 tons of soybeans per day.

Oil is to be leached from 100,000 kg/h of soybean flakes, containing 19 wt% oil, in a single equilibrium stage by 100,000 kg/h of a hexane solvent. Experimental data indicate that the oil content of the flakes will be reduced to 0.5 wt%. For the type of equipment to be used, the expected contents of the underflows is as follows:

|   |      |      |      |      |      |      |
|---|------|------|------|------|------|------|
| $\beta$ , Mass fraction of solids in underflow  | 0.68 | 0.67 | 0.65 | 0.62 | 0.58 | 0.53 |
| Mass ratio of solute in underflow liquid, $X_B$ | 0.0  | 0.2  | 0.4  | 0.6  | 0.8  | 1.0  |

Calculate, both graphically and analytically, compositions and flow rates of the underflow and overflow, assuming an ideal leaching stage. What % of oil in the feed is recovered?

#### Solution

The flakes contain  $(0.19)(100,000) = 19,000$  kg/h of oil and  $(100,000 - 19,000) = 81,000$  kg/h of insolubles. However, all of the oil is not leached. For convenience in the calculations, lump the unleached oil with the insolubles to give an effective A. The flow rate of unleached oil =  $(81,000)(0.5/99.5) = 407$  kg/h. Therefore, the flow rate of A is taken as  $(81,000 + 407) = 81,407$  kg/h and the oil in the feed is just the amount leached, or  $(19,000 - 407) =$

18,593 kg/h of B. Therefore, in the feed,  $F$ ,  $Y_A = (81,407/18,593) = 4.38$ , and  $X_B = 1.0$ .

The sum of the liquid solutions in the underflow and overflow includes 100,000 kg/h of hexane and 18,593 kg/h of leached oil. Therefore, for the underflow and overflow,  $X_B = Y_B = [18,593/(100,000 + 18,593)] = 0.157$ .

This is a case of variable-solution underflow. Using data in the above table, convert values of  $\beta$  to values of  $X_A$ ,

$$X_A = \frac{\text{kg/h A}}{\text{kg/h (B + C)}} = \frac{\beta U}{(1 - \beta)U} = \frac{\beta}{(1 - \beta)} \quad (1)$$

Using (1), the following values of  $X_A$  are computed from the previous table.

|       |      |      |      |      |      |      |
|-------|------|------|------|------|------|------|
| $X_A$ | 2.13 | 2.03 | 1.86 | 1.63 | 1.38 | 1.13 |
| $X_B$ | 0.0  | 0.2  | 0.4  | 0.6  | 0.8  | 1.0  |

### Graphical Method

Figure 4.21 is a plot of  $X_A$  as a function of  $X_B$ . Because no solids leave in the overflow, that line is horizontal at  $X_A = 0$ . Plotted are the feeds,  $F$ , and hexane,  $S$ , with a straight line between them. A point for the overflow,  $V$ , is plotted at  $X_A = 0$  and, from above,  $X_B = 0.157$ . Since  $Y_B = X_B = 0.157$ , the value of  $X_A$  in the underflow is at the intersection of a vertical line from overflow,  $V$ , to the underflow line. This value is  $X_A = 2.05$ . Lines  $\overline{FS}$  and  $\overline{UV}$  intersect at point  $M$ .

In the overflow, from  $X_B = 0.157$ , mass fractions of solute B and solvent C are, respectively, 0.157 and  $(1 - 0.157) = 0.843$ . In the underflow, using  $X_A = 2.05$  and  $X_B = 0.157$ , mass fractions of solids B and C are  $[2.05/(1 + 2.05)] = 0.672$ ,  $0.157(1 - 0.672) = 0.0515$ , and  $(1 - 0.672 - 0.0515) = 0.2765$ , respectively.

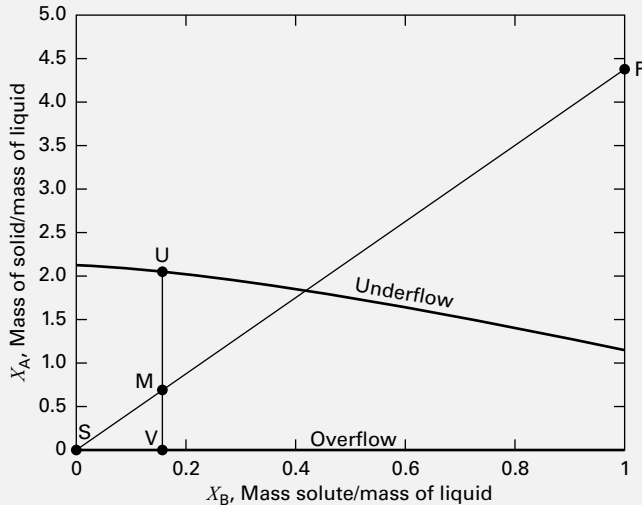


Figure 4.21 Constructions for Example 4.9.

The inverse-lever-arm rule is used to compute the underflow and overflow. The rule applies only to the liquid phases in the two exiting streams because Figure 4.21 is on a solids-free basis. The mass ratio of liquid flow rate in the underflow to liquid flow rate in the overflow is the ratio of line  $\overline{MV}$  to line  $\overline{MU}$ . With  $M$  located at  $X_A = 0.69$ , this ratio =  $(0.69 - 0.0)/(2.05 - 0.69) = 0.51$ . Thus, the liquid flow rate in the underflow =  $(100,000 + 18,593)(0.51)/(1 + 0.51) = 40,054$  kg/h. Adding the flow rates of carrier and unextracted oil gives  $U = 40,054 + 81,407 = 121,461$  kg/h or, say, 121,000 kg/h. The overflow rate =  $V = 200,000 - 121,000 = 79,000$  kg/h.

Oil flow rate in the feed is 19,000 kg/h. The oil flow rate in the overflow =  $Y_B V = 0.157(79,000) = 12,400$  kg/h. Thus, the oil in the feed that is recovered in the overflow =  $12,400/19,000 = 0.653$  or 65.3%. Adding washing stages, as described in §5.2, can increase the oil recovery.

### Algebraic Method

As with the graphical method,  $X_B = 0.157$ , giving a value from the previous table of  $X_A = 2.05$ . Then, since the flow rate of solids in the underflow = 81,407 kg/h, the flow rate of liquid in the underflow =  $81,407/2.05 = 39,711$  kg/h. The total flow rate of underflow is  $U = 81,407 + 39,711 = 121,118$  kg/h. By mass balance, the flow rate of overflow =  $200,000 - 121,118 = 78,882$  kg/h. These values are close to those obtained graphically. The percentage recovery of oil, and the underflow and overflow, are computed as before.

## §4.7.2 Crystallization

Crystallization takes place from aqueous or nonaqueous solutions. Consider a binary mixture of two organic chemicals such as naphthalene and benzene, whose solid-liquid equilibrium diagram at 1 atm is shown in Figure 4.22. Points A and B are melting (freezing) points of pure benzene ( $5.5^\circ\text{C}$ ) and pure naphthalene ( $80.2^\circ\text{C}$ ). When benzene is dissolved in liquid naphthalene or vice versa, the freezing point is depressed. Point E is the eutectic point, corresponding to a eutectic temperature ( $-3^\circ\text{C}$ ) and composition (80 wt% benzene). "Eutectic" is derived from a Greek word meaning "easily fused," and in Figure 4.22 it represents the binary mixture of naphthalene and benzene with the lowest freezing (melting) point.

Points located above the curve AEB correspond to a homogeneous liquid phase. Curve AE is the solubility curve for benzene in naphthalene. For example, at  $0^\circ\text{C}$  solubility is very high, 87 wt% benzene. Curve EB is the solubility curve for naphthalene in benzene. At  $25^\circ\text{C}$ , solubility is 41 wt% naphthalene and at  $50^\circ\text{C}$ , it is much higher. For most mixtures, solubility increases with temperature.

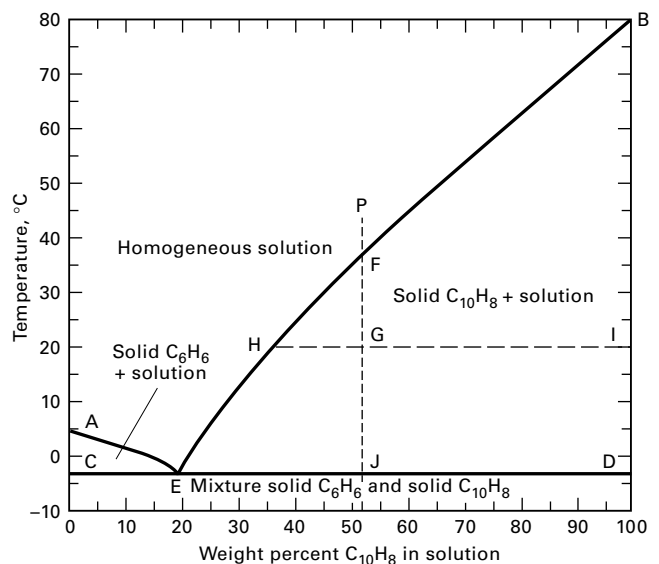


Figure 4.22 Solubility of naphthalene in benzene.

[Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part I*, 2nd ed., John Wiley & Sons, New York (1954).]

If a liquid solution represented by point P is cooled along the vertical dashed line, it remains liquid until the line intersects the solubility curve at point F.

If the temperature is lowered further, crystals of naphthalene form and the remaining liquid, the *mother liquor*, becomes richer in benzene. When point G is reached, pure naphthalene crystals and a mother liquor, point H on solubility curve EB, coexist, the solution composition being 37 wt% naphthalene. By the Gibbs phase rule,  $(4-1)$ , with  $C = 2$  and  $\mathcal{P} = 2$ ,  $\mathcal{F} = 2$ . Thus for fixed  $T$  and  $P$ , compositions are fixed. The fraction of solution crystallized can be determined by the inverse-lever-arm rule. In Figure 4.22, the fraction is  $\text{kg naphthalene crystals/kg original solution} = \text{length of line GH}/\text{length of line HI} = (52 - 37)/(100 - 37) = 0.238$ .

As the temperature is lowered, line CED, corresponding to the eutectic temperature, is reached at point J, where the two-phase system consists of naphthalene crystals and a mother liquor of eutectic composition E. Any further removal of heat causes the eutectic solution to solidify.

#### EXAMPLE 4.10 Crystallization of Naphthalene from a Solution with Benzene.

Eight thousand kg/h of a solution of 80 wt% naphthalene and 20 wt% benzene at 70°C is cooled to 30°C to form naphthalene crystals. If equilibrium is achieved, determine the kg of crystals formed and the composition in wt% of the mother liquor.

##### Solution

From Figure 4.22, at 30°C, the solubility of naphthalene is 45 wt%. By the inverse-lever-arm rule, for an original 80 wt% solution,

$$\frac{\text{kg naphthalene crystals}}{\text{kg original mixture}} = \frac{(80 - 45)}{(100 - 45)} = 0.636$$

The flow rate of crystals = 0.636 (8,000) = 5,090 kg/h.

The remaining 2,910 kg/h of mother liquor is 55 wt% benzene.

Crystallization of a salt from an aqueous solution can be complicated by the formation of water hydrates. These are stable, solid compounds that exist within certain temperature ranges. For example,  $\text{MgSO}_4$  forms the stable hydrates  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . The high hydrate exists at low temperatures; the low hydrate exists at higher temperatures.

A simpler example is that of  $\text{Na}_2\text{SO}_4$  and water. As seen in the phase diagram in Figure 4.23, only one stable hydrate is formed,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , known as Glauber's salt. Since the molecular weights are 142.05 for  $\text{Na}_2\text{SO}_4$  and 18.016 for  $\text{H}_2\text{O}$ , the weight percent  $\text{Na}_2\text{SO}_4$  in the decahydrate is 44.1, which is the vertical line BFG.

The water freezing point, 0°C, is at A, but the melting point of  $\text{Na}_2\text{SO}_4$ , 884°C, is not on the diagram. The decahydrate melts at 32.4°C, point B, to form solid  $\text{Na}_2\text{SO}_4$  and a mother liquor, point C, of 32.5 wt%  $\text{Na}_2\text{SO}_4$ . As  $\text{Na}_2\text{SO}_4$  dissolves in water, the freezing point is depressed slightly along curve AE until the eutectic, point E, is reached. Curves EC and CD represent solubilities of decahydrate crystals and anhydrous sodium sulfate in water. The solubility of  $\text{Na}_2\text{SO}_4$  decreases slightly with increasing temperature, which is unusual. In the region below GFBHI, a solid solution of anhydrous and decahydrate forms exist. The amounts of coexisting phases can be found by the inverse-lever-arm rule.

#### EXAMPLE 4.11 Crystallization of $\text{Na}_2\text{SO}_4$ from Water.

A 30 wt% aqueous  $\text{Na}_2\text{SO}_4$  solution of 5,000 lb/h enters a cooling-type crystallizer at 50°C. At what temperature will crystallization begin? Will the crystals be decahydrate or the anhydrous form? At what temperature will the mixture crystallize 50% of the  $\text{Na}_2\text{SO}_4$ ?

##### Solution

From Figure 4.23, the 30 wt%  $\text{Na}_2\text{SO}_4$  solution at 50°C corresponds to a point in the homogeneous liquid solution region. If a vertical

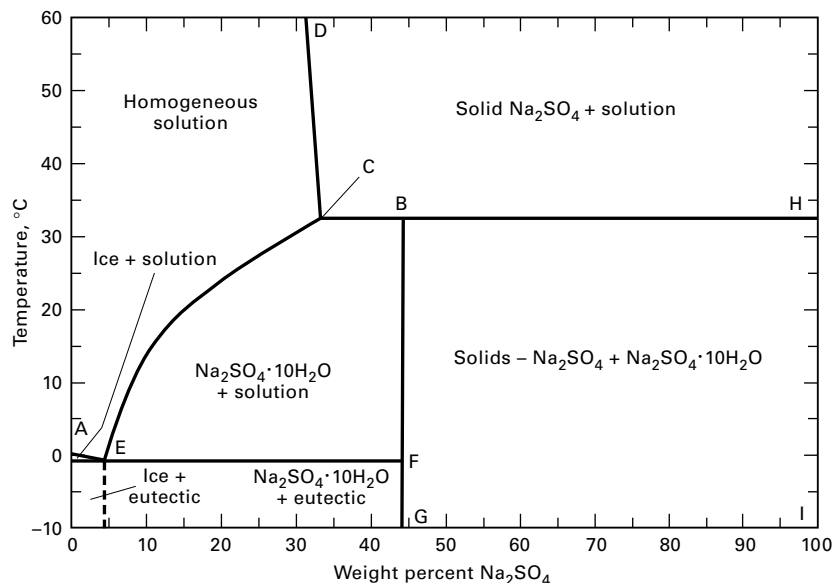


Figure 4.23 Solubility of sodium sulfate in water.

[Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part I*, 2nd ed., John Wiley & Sons, New York (1954).]

line is dropped from that point, it intersects solubility curve EC at 31°C. Below this temperature, the crystals are the decahydrate.

The feed contains  $(0.30)(5,000) = 1,500$  lb/h of  $\text{Na}_2\text{SO}_4$  and  $(5,000 - 1,500) = 3,500$  lb/h of  $\text{H}_2\text{O}$ . Thus,  $(0.5)(1,500) = 750$  lb/h are to be crystallized. The decahydrate crystals include water of hydration in an amount given by a ratio of molecular weights or

$$750 \left[ \frac{(10)(18.016)}{(142.05)} \right] = 950 \text{ lb/h}$$

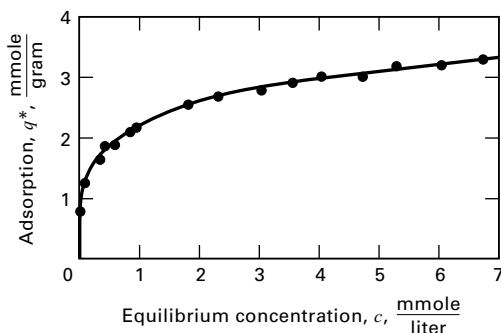
The total amount of decahydrate is  $750 + 950 = 1,700$  lb/h. The water remaining in the mother liquor is  $3,500 - 950 = 2,550$  lb/h. The composition of the mother liquor is  $750/(2,550 + 750)$  (100%) = 22.7 wt%  $\text{Na}_2\text{SO}_4$ . From Figure 4.23, the temperature corresponding to 22.7 wt%  $\text{Na}_2\text{SO}_4$  on the solubility curve EC is 26°C.

### §4.7.3 Liquid Adsorption

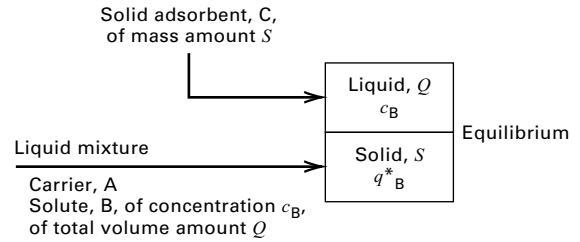
When a liquid contacts a microporous solid, adsorption takes place on the external and internal solid surfaces until equilibrium is reached. The solid *adsorbent* is essentially insoluble in the liquid. The component(s) adsorbed are called *solutes* when in the liquid and *adsorbates* upon adsorption. The higher the concentration of solute, the higher the adsorbate concentration on the adsorbent. Component(s) of the liquid other than the solute(s) are called the *solvent* or *carrier* and are assumed not to adsorb.

No theory for predicting adsorption-equilibrium curves, based on molecular properties of the solute and solid, is universally embraced, so laboratory measurements must be performed to provide data for plotting curves, called *adsorption isotherms*. Figure 4.24, taken from the data of Fritz and Schuluender [13], is an isotherm for the adsorption of phenol from an aqueous solution onto activated carbon at 20°C. Activated carbon is a microcrystalline, nongraphitic form of carbon, whose microporous structure gives it a high internal surface area per unit mass of carbon, and therefore a high capacity for adsorption. Activated carbon preferentially adsorbs organic compounds when contacted with water containing dissolved organics.

As shown in Figure 4.24, as the concentration of phenol in water increases, adsorption increases rapidly at first, then increases slowly. When the concentration of phenol is 1.0 mmol/L (0.001 mol/L of aqueous solution or 0.000001 mol/g of aqueous solution), the concentration of phenol on the activated carbon is somewhat more than 2.16 mmol/g (0.00216



**Figure 4.24** Adsorption isotherm for phenol from an aqueous solution in the presence of activated carbon at 20°C.



**Figure 4.25** Equilibrium stage for liquid adsorption.

mol/g of carbon or 0.203 g phenol/g of carbon). Thus, the affinity of this adsorbent for phenol is high. The extent of adsorption depends on the process used to produce the activated carbon. Adsorption isotherms can be used to determine the amount of adsorbent required to selectively remove a given amount of solute from a liquid.

Consider the ideal, single-stage adsorption process of Figure 4.25, where A is the carrier liquid, B is the solute, and C is the solid adsorbent. Let:  $c_B$  = concentration of solute in the carrier liquid, mol/unit volume;  $q_B$  = concentration of adsorbate, mol/unit mass of adsorbent;  $Q$  = volume of liquid (assumed to remain constant during adsorption); and  $S$  = mass of adsorbent (solute-free basis).

A solute material balance, assuming that the entering adsorbent is free of solute and that equilibrium is achieved, as designated by the asterisk superscript on  $q$ , gives

$$c_B^{(F)} Q = c_B Q = q_B^* S \quad (4-28)$$

This equation can be rearranged in the form of a straight line that can be plotted on a graph of the type in Figure 4.24 to obtain a graphical solution for  $c_B$  and  $q_B^*$ . Solving (4-28) for  $q_B^*$ ,

$$q_B^* = -\frac{Q}{S} c_B + c_B^{(F)} \frac{Q}{S} \quad (4-29)$$

The intercept on the  $c_B$  axis is  $c_B^{(F)} Q/S$ , and the slope is  $-(Q/S)$ . The intersection of (4-29) with the adsorption isotherm is the equilibrium condition  $c_B$  and  $q_B^*$ .

Alternatively, an algebraic solution can be obtained if the adsorption isotherm for equilibrium-liquid adsorption of a species  $i$  can be fitted to an equation. For example, the Freundlich equation discussed in Chapter 15 is of the form

$$q_i^* = A c_i^{(1/n)} \quad (4-30)$$

where  $A$  and  $n$  depend on the solute, carrier, and adsorbent. Constant,  $n$ , is greater than 1, and  $A$  is a function of temperature. Freundlich developed his equation from data on the adsorption on charcoal of organic solutes from aqueous solutions. Substitution of (4-30) into (4-29) gives

$$A c_B^{(1/n)} = -\frac{Q}{S} c_B + c_B^{(F)} \frac{Q}{S} \quad (4-31)$$

which is a nonlinear equation in  $c_B$  that is solved numerically by an iterative method, as illustrated in the following example.

#### EXAMPLE 4.12 Adsorption of Phenol on Activated Carbon.

A 1.0-liter solution of 0.010 mol of phenol in water is brought to equilibrium at 20°C with 5 g of activated carbon having the



adsorption isotherm shown in Figure 4.24. Determine the percent adsorption and equilibrium concentration of phenol on carbon by (a) a graphical method, and (b) a numerical algebraic method. For the latter case, the curve of Figure 4.24 is fitted with the Freundlich equation, (4-30), giving

$$q_B^* = 2.16c_B^{(1/4.35)} \quad (1)$$

### Solution

From the data,  $c_B^{(F)} = 10$  mmol/L,  $Q = 1$  L, and  $S = 5$  g.

#### (a) Graphical method.

From (4-29),  $q_B^* = -(\frac{1}{5})c_B + 10(\frac{1}{5}) = -0.2c_B + 2$ .

Plot this equation, with a slope of  $-0.2$  and an intercept of  $2$ , on Figure 4.24. An intersection with the equilibrium curve will occur at  $q_B^* = 1.9$  mmol/g and  $c_B = 0.57$  mmol/liter. Thus, the adsorption of phenol is

$$\frac{c_B^{(F)} - c_B}{c_B^{(F)}} = \frac{10 - 0.57}{10} = 0.94 \quad \text{or} \quad 94\%$$

#### (b) Numerical algebraic method.

Applying Eq. (1) from the problem statement and (4-31),

$$2.16c_B^{0.23} = -0.2c_B + 2 \quad (2)$$

$$\text{or} \quad f\{c_B\} = 2.16c_B^{0.23} + 0.2c_B - 2 = 0 \quad (3)$$

This nonlinear equation for  $c_B$  can be solved by an iterative numerical technique. For example, Newton's method [14], applied to Eq. (3), uses the iteration rule:

$$c_B^{(k+1)} = c_B^{(k)} - f^{(k)}\{c_B\}/f'^{(k)}\{c_B\} \quad (4)$$

where  $k$  is the iteration index. For this example,  $f\{c_B\}$  is given by Eq. (3) and  $f'\{c_B\}$  is obtained by differentiating with respect to  $c_B$ :

$$f'^{(k)}\{c_B\} = 0.497c_B^{-0.77} + 0.2$$

A convenient initial guess for  $c_B$  is 100% adsorption of phenol to give  $q_B^* = 2$  mmol/g. Then, from (4-30),  $c_B^{(0)} = (q_B^*/A)^n = (2/2.16)^{4.35} = 0.72$  mmol/L, where the (0) superscript designates the starting guess. The Newton iteration rule of Eq. (4-1) is now used, giving the following results:

| $k$ | $c_B^{(k)}$ | $f^{(k)}\{c_B\}$ | $f'^{(k)}\{c_B\}$ | $c_B^{(k+1)}$ |
|-----|-------------|------------------|-------------------|---------------|
| 0   | 0.72        | 0.1468           | 0.8400            | 0.545         |
| 1   | 0.545       | -0.0122          | 0.9928            | 0.558         |
| 2   | 0.558       | -0.00009         | 0.9793            | 0.558         |

These results indicate convergence to  $f\{c_B\} = 0$  for a value of  $c_B = 0.558$  after only three iterations. From Eq. (1),  $q_B^* = 2.16(0.558)^{(1/4.35)} = 1.89$  mmol/g. Numerical and graphical methods are in agreement.

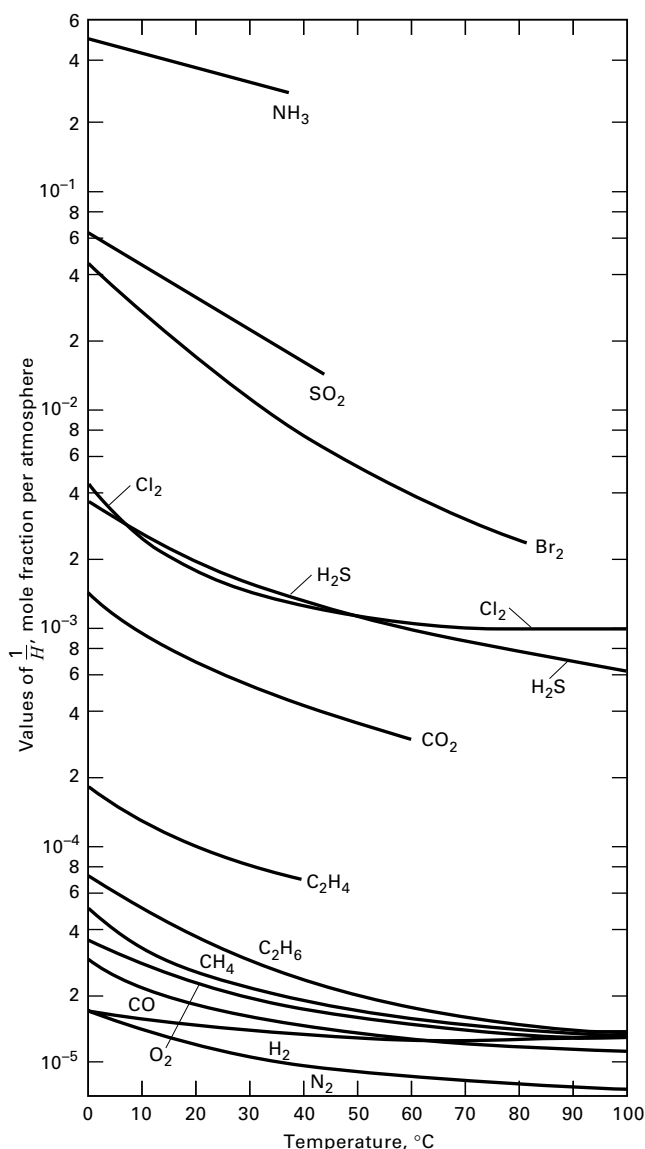
## §4.8 GAS-LIQUID SYSTEMS

Vapor-liquid systems were covered in § 4.2, 4.3, and 4.4, wherein the vapor was mostly condensable. Although the terms *vapor* and *gas* are often used interchangeably, the term *gas* often designates a mixture for which the ambient

temperature is above the critical temperatures of most or all of the species. Thus, in gas-liquid systems, the components of the gas are not easily condensed.

Even when components of a gas mixture are at a temperature above critical, they dissolve in a liquid solvent to an extent that depends on temperature and their partial pressure in the gas mixture. With good mixing, equilibrium between the two phases can be achieved in a short time unless the liquid is very viscous.

No widely accepted theory for gas-liquid solubilities exists. Instead, plots of experimental data, or empirical correlations, are used. Experimental data for 13 pure gases dissolved in water are plotted in Figure 4.26 over a range of temperatures from 0 to 100°C. The ordinate is the gas mole fraction in the liquid when gas pressure is 1 atm. The curves of Figure 4.26 can be used to estimate the solubility in water



**Figure 4.26** Henry's law constant for solubility of gases in water.

[Adapted from O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles. Part I*, 2nd ed., John Wiley & Sons, New York (1954).]

at other pressures and for mixtures of gases by applying Henry's law and using the partial pressure of the solute, provided that mole fractions are low and no chemical reactions occur in the gas or water. Henry's law, from Table 2.3, is rewritten for use with Figure 4.26 as

$$x_i = \left(\frac{1}{H_i}\right)y_iP \quad (4-32)$$

where  $H_i$  = Henry's law constant, atm.

For gases with a high solubility, such as ammonia, Henry's law is not applicable, even at low partial pressures. In that case, experimental data for the actual conditions of pressure and temperature are necessary. Calculations of equilibrium conditions are made, as in previous sections of this chapter, by combining material balances with equilibrium relationships.

#### EXAMPLE 4.13 Absorption of CO<sub>2</sub> with Water.

An ammonia plant, located at the base of a 300-ft-high mountain, employs a unique absorption system for disposing of byproduct CO<sub>2</sub>, in which the CO<sub>2</sub> is absorbed in water at a CO<sub>2</sub> partial pressure of 10 psi above that required to lift water to the top of the mountain. The CO<sub>2</sub> is then vented at the top of the mountain, the water being recirculated as shown in Figure 4.27. At 25°C, calculate the amount of water required to dispose of 1,000 ft<sup>3</sup> (STP) of CO<sub>2</sub>.

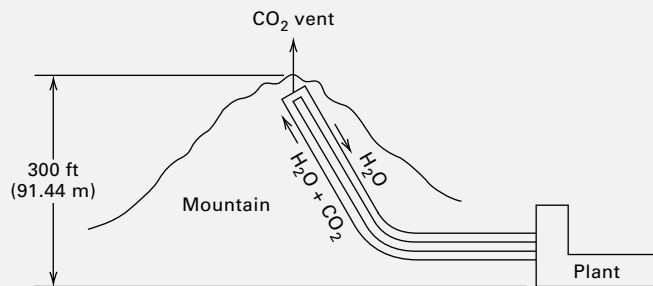


Figure 4.27 Flowsheet for Example 4.13.

#### Solution

Basis: 1,000 ft<sup>3</sup> of CO<sub>2</sub> at 0°C and 1 atm (STP). From Figure 4.26, the reciprocal of the Henry's law constant for CO<sub>2</sub> at 25°C is  $6 \times 10^{-4}$  mole fraction/atm CO<sub>2</sub> pressure in the absorber (at the foot of the mountain) is

$$p_{\text{CO}_2} = \frac{10}{14.7} + \frac{300 \text{ ft H}_2\text{O}}{34 \text{ ft H}_2\text{O}/\text{atm}} = 9.50 \text{ atm} = 960 \text{ kPa}$$

At this partial pressure, the concentration of CO<sub>2</sub> in the water is

$$x_{\text{CO}_2} = 9.50(6 \times 10^{-4}) = 5.7 \times 10^{-3} \text{ mole fraction CO}_2 \text{ in water}$$

The corresponding ratio of dissolved CO<sub>2</sub> to water is

$$\frac{5.7 \times 10^{-3}}{1 - 5.7 \times 10^{-3}} = 5.73 \times 10^{-3} \text{ mol CO}_2/\text{mol H}_2\text{O}$$

The total number of moles of CO<sub>2</sub> to be absorbed is

$$\frac{1,000 \text{ ft}^3}{359 \text{ ft}^3/\text{lbmol (at STP)}} = \frac{1,000}{359} = 2.79 \text{ lbmol}$$

or  $(2.79)(44)(0.454) = 55.73 \text{ kg}$ .

Assuming all absorbed CO<sub>2</sub> is vented, the number of moles of water required is  $2.79/(5.73 \times 10^{-3}) = 488 \text{ lbmol} = 8,730 \text{ lb} = 3,963 \text{ kg}$ .

If one corrects for the fact that not all the CO<sub>2</sub> is vented, because the pressure on top of the mountain is 101 kPa, 4,446 kg (9,810 lb) of water are required.

#### EXAMPLE 4.14 Equilibrium Diagram for Air–NH<sub>3</sub>–H<sub>2</sub>O at 20°C and 1 atm.

The partial pressure of ammonia (A) in air–ammonia mixtures in equilibrium with their aqueous solutions at 20°C is given in Table 4.7. Using these data, and neglecting the vapor pressure of water and the solubility of air in water, construct an equilibrium diagram at 101 kPa using mole ratios  $Y_A = \text{mol NH}_3/\text{mol air}$  and  $X_A = \text{mol NH}_3/\text{mol H}_2\text{O}$  as coordinates. Henceforth, the subscript A is dropped. If 10 mol of gas of  $Y = 0.3$  are contacted with 10 mol of solution of  $X = 0.1$ , what are the compositions of the resulting phases? The process is assumed to be isothermal at 1 atm.

Table 4.7 Partial Pressure of Ammonia over Ammonia–Water Solutions at 20°C

| NH <sub>3</sub> Partial Pressure, kPa | g NH <sub>3</sub> /g H <sub>2</sub> O |
|---------------------------------------|---------------------------------------|
| 4.23                                  | 0.05                                  |
| 9.28                                  | 0.10                                  |
| 15.2                                  | 0.15                                  |
| 22.1                                  | 0.20                                  |
| 30.3                                  | 0.25                                  |

#### Solution

Equilibrium data in Table 4.7 are recalculated in terms of mole ratios in Table 4.8 and plotted in Figure 4.28.

Table 4.8 Y–X Data for Ammonia–Water, 20°C

| Y, mol NH <sub>3</sub> /mol | X, mol NH <sub>3</sub> /mol |
|-----------------------------|-----------------------------|
| 0.044                       | 0.053                       |
| 0.101                       | 0.106                       |
| 0.176                       | 0.159                       |
| 0.279                       | 0.212                       |
| 0.426                       | 0.265                       |

Mol NH<sub>3</sub> in entering gas =  $10[Y/(1+Y)] = 10(0.3/1.3) = 2.3$

Mol NH<sub>3</sub> in entering liquid =  $10[X/(1+X)] = 10(0.1/1.1) = 0.91$

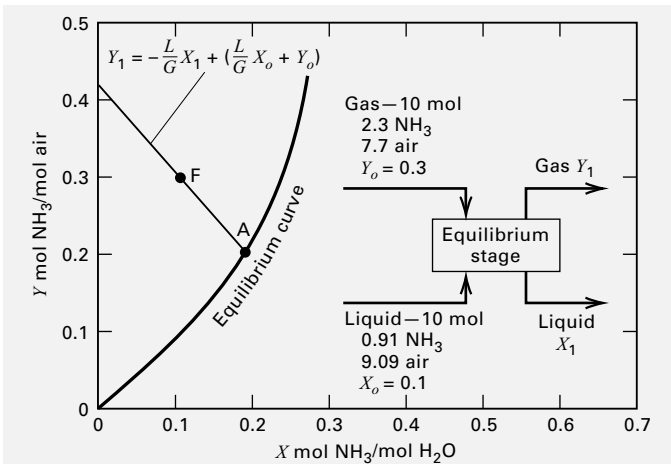
A material balance for ammonia about the equilibrium stage is

$$GY_0 + LX_0 = GY_1 + LX_1 \quad (1)$$

where  $G$  = moles of air and  $L$  = moles of H<sub>2</sub>O. Then  $G = 10 - 2.3 = 7.7 \text{ mol}$  and  $L = 10 - 0.91 = 9.09 \text{ mol}$ . Solving for  $Y_1$  from (1),

$$Y_1 = -\frac{L}{G}X_1 + \left(\frac{L}{G}X_0 + Y_0\right) \quad (2)$$

This is an equation of a straight line of slope  $(L/G) = -9.09/7.7 = -1.19$ , with an intercept of  $(L/G)X_0 + Y_0 = 0.42$ . The intersection of this material-balance line with the equilibrium curve, as shown in Figure 4.28, gives the ammonia composition of the gas and liquid leaving the stage as  $Y_1 = 0.195$  and  $X_1 = 0.19$ . This result can be checked by an NH<sub>3</sub> balance, since the amount of NH<sub>3</sub> leaving is



**Figure 4.28** Equilibrium for air–NH<sub>3</sub>–H<sub>2</sub>O at 20°C, 1 atm, in Example 4.14.

$(0.195)(7.70) + (0.19)(9.09) = 3.21$ , which equals the total moles of NH<sub>3</sub> entering.

Equation (2), the material-balance line, called an *operating line* and discussed in detail in Chapters 5 to 8, is the locus of all passing stream pairs; thus,  $X_0$ ,  $Y_0$  (point F) also lies on this operating line.

## §4.9 GAS–SOLID SYSTEMS

Gas–solid systems are encountered in sublimation, desublimation, and adsorption separation operations.

### §4.9.1 Sublimation and Desublimation

In sublimation, a solid vaporizes into a gas phase without passing through a liquid state. In desublimation, one or more components (solutes) in the gas phase are condensed to a solid phase without passing through a liquid state. At low pressure, both sublimation and desublimation are governed by the solid vapor pressure of the solute. Sublimation of the solid takes place when the partial pressure of the solute in the gas phase is less than the vapor pressure of the solid at the system temperature. When the partial pressure of the solute in the gas phase exceeds the vapor pressure of the solid, desublimation occurs. At equilibrium, the vapor pressure of the species as a solid is equal to the partial pressure of the species as a solute in the gas phase.

#### EXAMPLE 4.15 Desublimation of Phthalic Anhydride.

*Ortho*-xylene is completely oxidized in the vapor phase with air to produce phthalic anhydride, PA, in a catalytic reactor at about 370°C and 780 torr. A large excess of air is used to keep the xylene concentration below 1 mol% to avoid an explosive mixture. In a plant, 8,000 lbmol/h of reactor-effluent gas, containing 67 lbmol/h of PA and other amounts of N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, and water vapor, are cooled to separate the PA by desublimation to a solid at a total pressure of 770 torr. If the gas is cooled to 206°F, where the vapor pressure of solid PA is 1 torr, calculate the number of pounds of PA

condensed per hour as a solid, and the percent recovery of PA from the gas if equilibrium is achieved.

#### Solution

At these conditions, only PA condenses. The partial pressure of PA is equal to the vapor pressure of solid PA, or 1 torr. Thus, PA in the cooled gas is given by Dalton's law of partial pressures:

$$(n_{\text{PA}})_G = \frac{P_{\text{PA}}}{P} n_G \quad (1)$$

$$\text{where } n_G = (8,000 - 67) + (n_{\text{PA}})_G \quad (2)$$

and  $n = \text{lbmol/h}$ . Combining Eqs. (1) and (2),

$$\begin{aligned} (n_{\text{PA}})_G &= \frac{P_{\text{PA}}}{P} [(8,000 - 67) + (n_{\text{PA}})_G] \\ &= \frac{1}{770} [(8,000 - 67) + (n_{\text{PA}})_G] \end{aligned} \quad (3)$$

Solving this linear equation gives  $(n_{\text{PA}})_G = 10.3 \text{ lbmol/h}$  of PA.

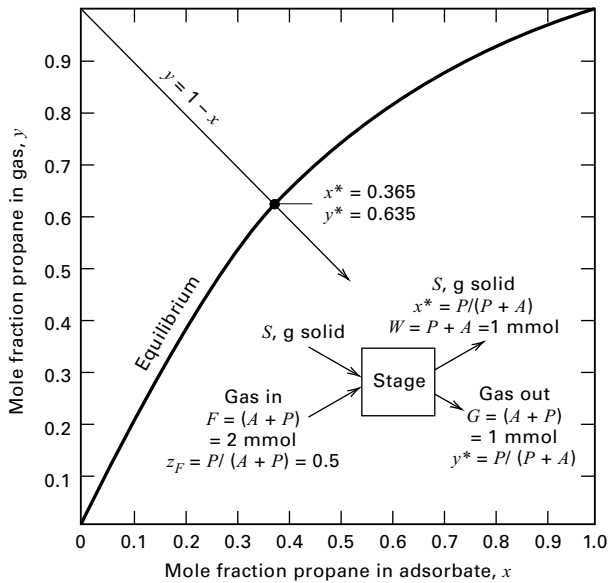
The amount of PA desublimed is  $67 - 10.3 = 56.7 \text{ lbmol/h}$ . The percent recovery of PA is  $56.7/67 = 0.846$  or 84.6%. The amount of PA remaining in the gas is above EPA standards, so a lower temperature is required. At 140°F the recovery is almost 99%.

### §4.9.2 Gas Adsorption

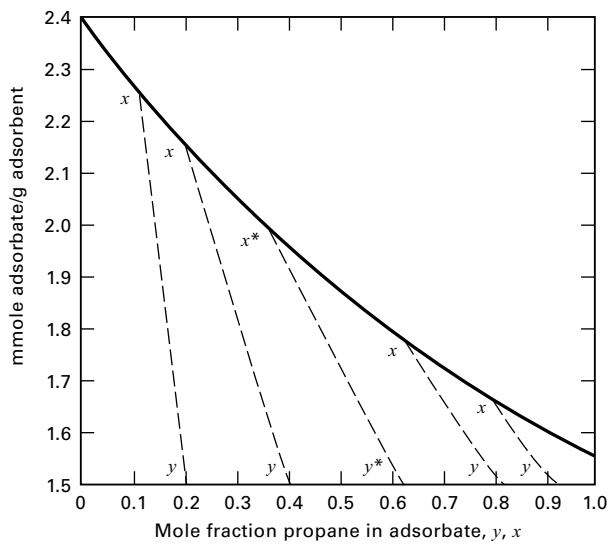
As with liquid mixtures, one or more components of a gas can be adsorbed on the external and internal surfaces of a porous, solid adsorbent. Data for a single solute can be represented by an adsorption isotherm of the type shown in Figure 4.24 or in similar diagrams. However, when two components of a gas mixture are adsorbed and the purpose is to separate them, other methods of representing the data, such as Figure 4.29, are preferred. Figure 4.29 displays the data of Lewis et al. [15] for the adsorption of a propane (P)–propylene (A) gas mixture on silica gel at 25°C and 101 kPa. At 25°C, a pressure of at least 1,000 kPa is required to initiate condensation of a mixture of propylene and propane. However, in the presence of silica gel, significant amounts of gas are adsorbed at 101 kPa.

Figure 4.29a is similar to a binary vapor–liquid plot of the type seen in §4.2. For adsorption, the liquid-phase mole fraction is replaced by the mole fraction in the adsorbate. For propylene–propane mixtures, propylene is adsorbed more strongly. For example, for an equimolar mixture in the gas phase, the adsorbate contains only 27 mol% propane. Figure 4.29b combines data for the mole fractions in the gas and adsorbate with the amount of adsorbate per unit of adsorbent. The mole fractions are obtained by reading the abscissa at the two ends of a tie line. With  $y_P = y^* = 0.50$ , Figure 4.29b gives  $x_P = x^* = 0.27$  and 2.08 mmol of adsorbate/g adsorbent. Therefore,  $y_A = 0.50$ , and  $x_A = 0.73$ . The separation factor, analogous to  $\alpha$  for distillation, is  $(0.50/0.27)/(0.50/0.73) = 2.7$ .

This value is much higher than the  $\alpha$  for distillation, which, from Figure 2.4 at 25°C and 1,100 kPa, is only 1.13. Accordingly, the separation of propylene and propane by adsorption has received some attention.



(a)



(b)

**Figure 4.29** Adsorption equilibrium at 25°C and 101 kPa of propane and propylene on silica gel.

[Adapted from W.K. Lewis, E.R. Gilliland, B. Chertow, and W. H. Hoffman, *J. Am. Chem. Soc.*, **72**, 1153 (1950).]

#### EXAMPLE 4.16 Separation of Propylene-Propane by Adsorption.

Propylene (A) and propane (P) are separated by preferential adsorption on porous silica gel (S) at 25°C and 101 kPa. Two millimoles of a gas of 50 mol% P and 50 mol% A are equilibrated with silica gel at 25°C and 101 kPa. Measurements show that 1 mmol of gas is adsorbed. If the data of Figure 4.29 apply, what is the mole fraction of propane in the equilibrium gas and in the adsorbate, and how many grams of silica gel are used?

#### Solution

The process is represented in Figure 4.29a, where  $W$  = millimoles of adsorbate,  $G$  = millimoles of gas leaving, and  $z_F$  = mole fraction

of propane in the feed. The propane mole balance is

$$Fz_F = Wx^* + Gy^* \quad (1)$$

Because  $F = 2$ ,  $z_F = 0.5$ ,  $W = 1$ , and  $G = F - W = 1$ ,  $1 = x^* + y^*$ . The operating (material-balance) line  $y^* = 1 - x^*$  in Figure 4-29a is the locus of all solutions of the material-balance equations. It intersects the equilibrium curve at  $x^* = 0.365$ ,  $y^* = 0.635$ . From Figure 4.29b, at the point  $x^*$ , there are 2.0 mmol adsorbate/g adsorbent and  $1.0/2 = 0.50$  g of silica gel.

## §4.10 MULTIPHASE SYSTEMS

Although two-phase systems predominate, at times three or more co-existing phases are encountered. Figure 4.30 is a schematic of a photograph of a laboratory curiosity taken from Hildebrand [16], which shows seven phases in equilibrium. The phase on top is air, followed by six liquid phases in order of increasing density: hexane-rich, aniline-rich, water-rich, phosphorous, gallium, and mercury. Each phase contains all components in the mixture, but many of the mole fractions are extremely small. For example, the aniline-rich phase contains on the order of 10 mol% *n*-hexane, 20 mol% water, but much less than 1 mol% each of dissolved air, phosphorous, gallium, and mercury. Note that even though the hexane-rich phase is not in direct contact with the water-rich phase, water (approximately 0.06 mol %) is present in the hexane-rich phase because each phase is in equilibrium with each of the other phases, by the equality of component fugacities:

$$f_i^{(1)} = f_i^{(2)} = f_i^{(3)} = f_i^{(4)} = f_i^{(5)} = f_i^{(6)} = f_i^{(7)}$$

More practical multiphase systems include the vapor-liquid-solid systems present in evaporative crystallization and pervaporation, and the vapor-liquid-liquid systems that occur when distilling certain mixtures of water and hydrocarbons that have a limited solubility in water. Actually, all of the two-phase systems considered in this chapter involve a third phase, the containing vessel. However, as a practical matter, the container is selected on the basis of its chemical inertness and insolubility.

Although calculations of multiphase equilibria are based on the same principles as for two-phase systems (material

|                              |
|------------------------------|
| Air                          |
| <i>n</i> -hexane-rich liquid |
| Aniline-rich liquid          |
| Water-rich liquid            |
| Phosphorous liquid           |
| Gallium liquid               |
| Mercury liquid               |

**Figure 4.30** Seven phases in equilibrium.

balances, energy balances, and equilibrium), the computations are complex unless assumptions are made, in which case approximate answers result. Rigorous calculations are best made with process simulators.

#### §4.10.1 Approximate Method for a Vapor–Liquid–Solid System

A simple case of multiphase equilibrium occurs in an evaporative crystallizer involving crystallization of an inorganic compound, B, from its aqueous solution at its bubble point in the presence of water vapor. Assume that only two components are present, B and water, that the liquid is a mixture of water and B, and that the solid is pure B. Then, the solubility of B in the liquid is not influenced by the presence of the vapor, and the system pressure at a given temperature can be approximated by Raoult's law applied to the liquid phase:

$$P = P_{\text{H}_2\text{O}}^s x_{\text{H}_2\text{O}} \quad (4-33)$$

where  $x_{\text{H}_2\text{O}}$  can be obtained from the solubility of B.

#### EXAMPLE 4.17 Evaporative Crystallizer.

A 5,000-lb batch of 20 wt% aqueous  $\text{MgSO}_4$  solution is fed to an evaporative crystallizer operating at 160°F. At this temperature, the stable solid phase is the monohydrate, with a  $\text{MgSO}_4$  solubility of 36 wt%. If 75% of the water is evaporated, calculate: (a) lb of water evaporated; (b) lb of monohydrate crystals,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; and (c) crystallizer pressure.

#### Solution

(a) The feed solution is  $0.20(5,000) = 1,000$  lb  $\text{MgSO}_4$ , and  $5,000 - 1,000 = 4,000$  lb  $\text{H}_2\text{O}$ . The amount of water evaporated is  $0.75(4,000) = 3,000$  lb  $\text{H}_2\text{O}$ .

(b) Let  $W$  = amount of  $\text{MgSO}_4$  remaining in solution. Then  $\text{MgSO}_4$  in the crystals =  $1,000 - W$ . MW of  $\text{H}_2\text{O}$  = 18 and MW of  $\text{MgSO}_4 = 120.4$ . Water of crystallization for the monohydrate =  $(1,000 - W)(18/120.4) = 0.15(1,000 - W)$ .

Water remaining in solution =  $4,000 - 3,000 - 0.15(1,000 - W) = 850 + 0.15W$ .

Total amount of solution remaining =  $850 + 0.15W + W = 850 + 1.15W$ . From the solubility of  $\text{MgSO}_4$ ,

$$0.36 = \frac{W}{850 + 1.15W}$$

Solving:  $W = 522$  pounds of dissolved  $\text{MgSO}_4$ .  $\text{MgSO}_4$  crystallized =  $1,000 - 522 = 478$  lb. Water of crystallization =  $0.15(1,000 - W) = 0.15(1,000 - 522) = 72$  lb.

Total monohydrate crystals =  $478 + 72 = 550$  lb.

(c) Crystallizer pressure is given by (4-33). At 160°F, the vapor pressure of  $\text{H}_2\text{O}$  is 4.74 psia. Then water remaining in solution =  $(850 + 0.15W)/18 = 51.6$  lbmol.

$\text{MgSO}_4$  remaining in solution =  $522/120.4 = 4.3$  lbmol. Hence,

$$x_{\text{H}_2\text{O}} = 51.6/(51.6 + 4.3) = 0.923.$$

By Raoult's law,  $p_{\text{H}_2\text{O}} = P = 4.74(0.923) = 4.38$  psia.

#### §4.10.2 Approximate Method for a Vapor–Liquid–Liquid System

Suitable for an approximate method is the case of a mixture containing water and hydrocarbons (HCs), at conditions such that a vapor and two liquid phases, HC-rich (1) and water-rich (2), coexist. Often the solubilities of water in the liquid HC phase and the HCs in the water phase are less than 0.1 mol% and may be neglected. Then, if the liquid HC phase obeys Raoult's law, system pressure is the sum of pressures of the liquid phases:

$$P = P_{\text{H}_2\text{O}}^s + \sum_{\text{HCs}} P_i^s x_i^{(1)} \quad (4-34)$$

For more general cases, at low pressures where the vapor phase is ideal but the liquid HC phase may be nonideal,

$$P = P_{\text{H}_2\text{O}}^s + P \sum_{\text{HCs}} K_i x_i^{(1)} \quad (4-35)$$

which can be rearranged to

$$P = \frac{P_{\text{H}_2\text{O}}^s}{1 - \sum_{\text{HCs}} K_i x_i^{(1)}} \quad (4-36)$$

Equations (4-34) and (4-36) can be used to estimate the pressure for a given temperature and liquid-phase composition, or iteratively to estimate the temperature for a given pressure. Of importance is the determination of which of six possible phase combinations are present:  $V$ ,  $V-L^{(1)}$ ,  $V-L^{(1)}-L^{(2)}$ ,  $V-L^{(2)}$ ,  $L^{(1)}-L^{(2)}$ , and  $L$ . Indeed, if a  $V-L^{(1)}-L^{(2)}$  solution to a problem exists,  $V-L^{(1)}$  and  $V-L^{(2)}$  solutions also almost always exist. In that case, the three-phase solution is the correct one. It is important, therefore, to seek the three-phase solution first.

#### EXAMPLE 4.18 Approximate Vapor–Liquid–Liquid Equilibrium.

A mixture of 1,000 kmol of 75 mol% water and 25 mol%  $n$ -octane is cooled under equilibrium conditions at a constant pressure of 133.3 kPa from a temperature of 136°C to a temperature of 25°C. Determine: (a) the initial phase condition, and (b) the temperature, phase amounts, and compositions when each phase change occurs. Assume that water and  $n$ -octane are immiscible liquids. The vapor pressure of octane is included in Figure 2.3.

#### Solution

(a) Initial phase conditions are  $T = 136^\circ\text{C} = 276.8^\circ\text{F}$  and  $P = 133.3$  kPa = 19.34 psia; vapor pressures are  $P_{\text{H}_2\text{O}}^s = 46.7$  psia and  $P_{n\text{C}_8}^s = 19.5$  psia. Because the initial pressure is less than the vapor pressure of each component, the initial phase condition is all vapor, with partial pressures

$$p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}} P = 0.75(19.34) = 14.5 \text{ psia}$$

$$p_{n\text{C}_8} = y_{n\text{C}_8} P = 0.25(19.34) = 4.8 \text{ psia}$$

(b) As the temperature is decreased, a phase change occurs when either  $P_{\text{H}_2\text{O}}^s = p_{\text{H}_2\text{O}} = 14.5$  psia or  $P_{n\text{C}_8}^s = p_{n\text{C}_8} = 4.8$  psia. The temperatures where these vapor pressures occur are 211°F for  $\text{H}_2\text{O}$  and 194°F for  $n\text{C}_8$ . The highest temperature applies.

Therefore, water condenses first when the temperature reaches 211°F. This is the dew-point temperature of the mixture at the system pressure. As the temperature is further reduced, the number of moles of water in the vapor decreases, causing the partial pressure of water to decrease below 14.5 psia and the partial pressure of  $nC_8$  to increase above 4.8 psia. Thus,  $nC_8$  begins to condense, forming a second liquid at a temperature higher than 194°F but lower than 211°F. This temperature, referred to as the *secondary dew point*, must be determined iteratively. The calculation is simplified if the bubble point of the mixture is computed first.

From (4-34),

$$P = 19.34 \text{ psi} = P_{H_2O}^s + P_{nC_8}^s \quad (1)$$

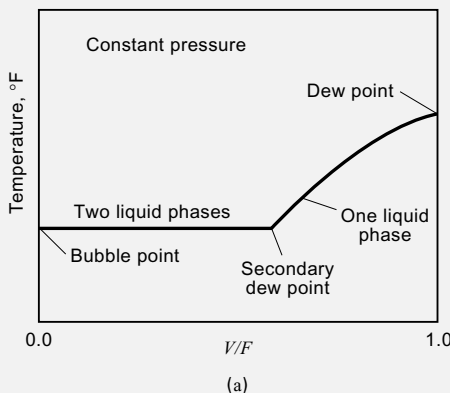
Thus, a temperature that satisfies (4-17) is sought:

| $T, ^\circ\text{F}$ | $P_{H_2O}^s, \text{psia}$ | $P_{nC_8}^s, \text{psia}$ | $P, \text{psia}$ |
|---------------------|---------------------------|---------------------------|------------------|
| 194                 | 10.17                     | 4.8                       | 14.97            |
| 202                 | 12.01                     | 5.6                       | 17.61            |
| 206                 | 13.03                     | 6.1                       | 19.13            |
| 207                 | 13.30                     | 6.2                       | 19.50            |

By interpolation,  $T = 206.7^\circ\text{F}$  for  $P = 19.34 \text{ psia}$ . Below  $206.7^\circ\text{F}$  the vapor phase disappears and only two immiscible liquids exist.

To determine the temperature at which one of the liquid phases disappears (the same condition as when the second liquid phase begins to appear, i.e., the secondary dew point), it is noted for this case, with only pure water and a pure HC present, that vaporization starting from the bubble point is at a constant temperature until one of the two liquid phases is completely vaporized. Thus, the secondary dew-point temperature is the same as the bubble-point temperature, or  $206.7^\circ\text{F}$ . At the secondary dew point, partial pressures are  $p_{H_2O} = 13.20 \text{ psia}$  and  $p_{nC_8} = 6.14 \text{ psia}$ , with all of the  $nC_8$  in the vapor. Therefore,

| Component        | Vapor |       | H <sub>2</sub> O-Rich Liquid |
|------------------|-------|-------|------------------------------|
|                  | kmol  | $y$   | kmol                         |
| H <sub>2</sub> O | 53.9  | 0.683 | 21.1                         |
| $nC_8$           | 25.0  | 0.317 | 0.0                          |
|                  | 78.9  | 1.000 | 21.1                         |



If desired, additional flash calculations can be made for conditions between the dew point and the secondary dew point. The resulting flash curve is shown in Figure 4.31a. If more than one HC species is present, the liquid HC phase does not evaporate at a constant composition and the secondary dew-point temperature is higher than the bubble-point temperature. Then the flash is described by Figure 4.31b.

### §4.10.3 Rigorous Method for a Vapor–Liquid–Liquid System

The rigorous method for treating a vapor–liquid–liquid system at a given temperature and pressure is called a *three-phase isothermal flash*. As first presented by Henley and Rosen [17], it is analogous to the isothermal two-phase flash algorithm in §4.4. The system is shown in Figure 4.32. The usual material balances and phase-equilibrium relations apply for each component:

$$Fz_i = Vy_i + L^{(1)}x_i^{(1)} + L^{(2)}x_i^{(2)} \quad (4-37)$$

$$K_i^{(1)} = y_i/x_i^{(1)} \quad (4-38)$$

$$K_i^{(2)} = y_i/x_i^{(2)} \quad (4-39)$$

A relation that can be substituted for (4-38) or (4-39) is

$$K_{D_i} = x_i^{(1)}/x_i^{(2)} \quad (4-40)$$

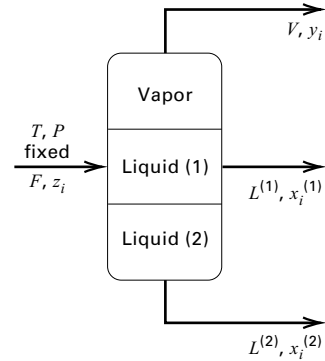


Figure 4.32 Conditions for a three-phase isothermal flash.

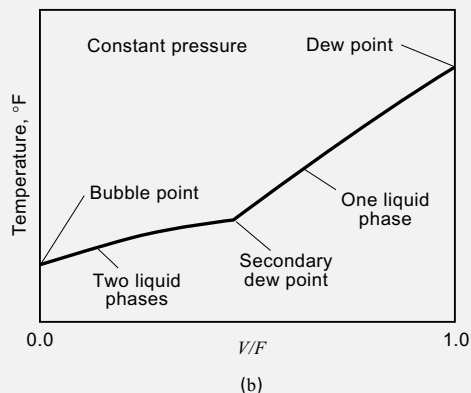


Figure 4.31 Typical flash curves for immiscible liquid mixtures of water and hydrocarbons at constant pressure: (a) only one hydrocarbon species present; (b) more than one hydrocarbon species present.

These equations are solved by a modification of the Rachford–Rice procedure if we let  $\Psi = V/F$  and  $\xi = L^{(1)}/(L^{(1)} + L^{(2)})$ , where  $0 \leq \Psi \leq 1$  and  $0 \leq \xi \leq 1$ . By combining (4-37), (4-38), and (4-39) with

$$\sum x_i^{(1)} - \sum y_i = 0 \quad (4-41)$$

and 
$$\sum x_i^{(1)} - \sum x_i^{(2)} = 0 \quad (4-42)$$

to eliminate  $y_i$ ,  $x_i^{(1)}$ , and  $x_i^{(2)}$ , two simultaneous equations in  $\Psi$  and  $\xi$  are obtained:

$$\sum_i \frac{z_i(1 - K_i^{(1)})}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)K_i^{(1)}/K_i^{(2)} + \Psi K_i^{(1)}} = 0 \quad (4-43)$$

and

$$\sum_i \frac{z_i(1 - K_i^{(1)}/K_i^{(2)})}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)K_i^{(1)}/K_i^{(2)} + \Psi K_i^{(1)}} = 0 \quad (4-44)$$

Values of  $\Psi$  and  $\xi$  are computed by solving nonlinear equations (4-43) and (4-44) simultaneously. Then the phase amounts and compositions are determined from

$$V = \Psi F \quad (4-45)$$

$$L^{(1)} = \xi(F - V) \quad (4-46)$$

$$L^{(2)} = F - V - L^{(1)} \quad (4-47)$$

$$y_i = \frac{z_i}{\xi(1 - \Psi)/K_i^{(1)} + (1 - \Psi)(1 - \xi)/K_i^{(2)} + \Psi} \quad (4-48)$$

$$x_i^{(1)} = \frac{z_i}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)(K_i^{(1)}/K_i^{(2)}) + \Psi K_i^{(1)}} \quad (4-49)$$

$$x_i^{(2)} = \frac{z_i}{\xi(1 - \Psi)(K_i^{(2)}/K_i^{(1)}) + (1 - \Psi)(1 - \xi) + \Psi K_i^{(2)}} \quad (4-50)$$

Calculations for a three-phase flash are difficult because of the strong dependency of  $K$ -values on liquid-phase compositions when two immiscible liquids are present. This dependency appears in the liquid-phase activity coefficients (e.g., Eq. (4) in Table 2.3). In addition, it is not obvious how many phases will be present. A typical algorithm for determining phase conditions is shown in Figure 4.33. Calculations are best made with a process simulator, which can also perform adiabatic or nonadiabatic three-phase flashes by iterating on temperature until the enthalpy balance,

$$h_F F + Q = h_V V + h_{L^{(1)}} L^{(1)} + h_{L^{(2)}} L^{(2)} = 0 \quad (4-51)$$

is satisfied.

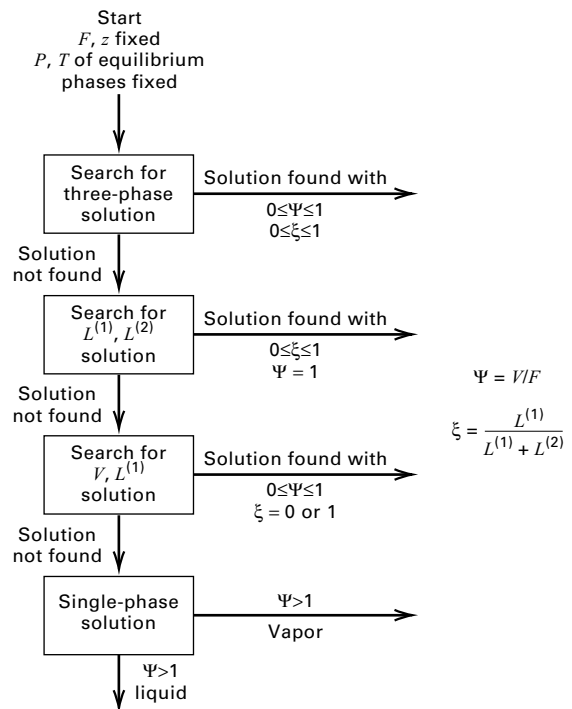


Figure 4.33 Algorithm for an isothermal three-phase flash.

#### EXAMPLE 4.19 Three-Phase Isothermal Flash.

In a process for producing styrene from toluene and methanol, the gaseous reactor effluent is as follows:

| Component    | kmol/h |
|--------------|--------|
| Hydrogen     | 350    |
| Methanol     | 107    |
| Water        | 491    |
| Toluene      | 107    |
| Ethylbenzene | 141    |
| Styrene      | 350    |

If this stream is brought to equilibrium at 38°C and 300 kPa. Compute the amounts and compositions of the phases present.

#### Solution

Because water, hydrocarbons, an alcohol, and a light gas are present, the possibility of a vapor and two liquid phases exists, with methanol distributed among all phases. The isothermal three-phase flash module of the CHEMCAD process simulator was used with Henry's law for H<sub>2</sub> and UNIFAC for activity coefficients for the other components, to obtain:

| Component    | kmol/h |                  |                  |
|--------------|--------|------------------|------------------|
|              | V      | L <sup>(1)</sup> | L <sup>(2)</sup> |
| Hydrogen     | 349.96 | 0.02             | 0.02             |
| Methanol     | 9.54   | 14.28            | 83.18            |
| Water        | 7.25   | 8.12             | 475.63           |
| Toluene      | 1.50   | 105.44           | 0.06             |
| Ethylbenzene | 0.76   | 140.20           | 0.04             |
| Styrene      | 1.22   | 348.64           | 0.14             |
| Totals       | 370.23 | 616.70           | 559.07           |

As expected, little  $H_2$  is dissolved in either liquid. The water-rich liquid phase,  $L^{(2)}$ , contains little of the hydrocarbons, but much methanol. The organic-rich phase,  $L^{(1)}$ , contains most of the hydrocarbons and small amounts of water and methanol. Additional calculations at 300 kPa indicate that the organic phase condenses first, with a dew point = 143°C and a secondary dew point = 106°C.

## SUMMARY

1. The Gibbs phase rule applies to intensive variables at equilibrium. It determines the number of independent variables that can be specified. This rule can be extended to determine the degrees of freedom (number of allowable specifications) for flow systems, including extensive variables. The intensive and extensive variables are related by material- and energy-balance equations and phase-equilibria data.
2. Vapor–liquid equilibrium conditions for binary systems can be represented by  $T$ – $y$ – $x$ ,  $y$ – $x$ , and  $P$ – $x$  diagrams. Relative volatility for a binary system tends to 1.0 as the critical point is approached.
3. Minimum- or maximum-boiling azeotropes formed by nonideal liquid mixtures are represented by the same types of diagrams used for nonazeotropic (zeotropic) binary mixtures. Highly nonideal liquid mixtures can form heterogeneous azeotropes having two liquid phases.
4. For multicomponent mixtures, vapor–liquid equilibrium-phase compositions and amounts can be determined by isothermal-flash, adiabatic-flash, and bubble- and dew-point calculations. For non-ideal mixtures, process simulators should be used.
5. Liquid–liquid equilibrium conditions for ternary mixtures are best determined graphically from triangular and other equilibrium diagrams, unless only one of the three components (the solute) is soluble in the two liquid phases. In that case, the conditions can be readily determined algebraically using phase-distribution ratios (partition coefficients) for the solute.
6. Liquid–liquid equilibrium conditions for multi-component mixtures of four or more components are best determined with process simulators, particularly when the system is not dilute in the solute(s).
7. Solid–liquid equilibrium occurs in leaching, crystallization, and adsorption. In leaching it is common to assume that all solute is dissolved in the solvent and that the remaining solid in the underflow is accompanied by a known fraction of liquid. Crystallization calculations are best made with a phase-equilibrium diagram. For crystallization of salts from an aqueous solution, formation of hydrates must be considered. Adsorption can be represented algebraically or graphically by adsorption isotherms.
8. Solubility of gases that are only sparingly soluble in a liquid are well represented by a Henry's law constant that depends on temperature.
9. Solid vapor pressure can determine equilibrium sublimation and desublimation conditions for gas–solid systems. Adsorption isotherms and  $y$ – $x$  diagrams are useful in adsorption-equilibrium calculations for gas mixtures in the presence of solid adsorbent.
10. Calculations of multiphase equilibrium are best made by process simulators. However, manual procedures are available for vapor–liquid–solid systems when no component is found in all phases, and to vapor–liquid–liquid systems when only one component distributes in all phases.

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## STUDY QUESTIONS

- 4.1. What two types of equations are used for single equilibrium stage calculations?
- 4.2. How do intensive and extensive variables differ?
- 4.3. What is meant by the number of degrees of freedom?
- 4.4. What are the limitations of the Gibbs phase rule? How can it be extended?
- 4.5. When a liquid and a vapor are in physical equilibrium, why is the vapor at its dew point and the liquid at its bubble point?
- 4.6. What is the difference between a homogeneous and a heterogeneous azeotrope?
- 4.7. Why do azeotropes limit the degree of separation achievable in a distillation operation?
- 4.8. What is the difference between an isothermal and an adiabatic flash?
- 4.9. Why is the isothermal-flash calculation so important?
- 4.10. When a binary feed is contacted with a solvent to form two equilibrium liquid phases, which is the extract and which the raffinate?
- 4.11. Why are triangular diagrams useful for ternary liquid–liquid equilibrium calculations? On such a diagram, what are the miscibility boundary, plait point, and tie lines?

- 4.12. Why is the right-triangular diagram easier to construct and read than an equilateral-triangular diagram? What is, perhaps, the only advantage of the latter diagram?
- 4.13. What are the conditions for an ideal, equilibrium leaching stage?
- 4.14. In crystallization, what is a eutectic? What is mother liquor? What are hydrates?
- 4.15. What is the difference between adsorbent and adsorbate?
- 4.16. In adsorption, why are adsorbents having a microporous structure desirable?
- 4.17. Does a solid have a vapor pressure?
- 4.18. What is the maximum number of phases that can exist at physical equilibrium for a given number of components?
- 4.19. In a rigorous vapor–liquid–liquid equilibrium calculation (the so-called three-phase flash), is it necessary to consider all possible phase conditions, i.e., all-liquid, all-vapor, vapor–liquid, liquid–liquid, as well as vapor–liquid–liquid?
- 4.20. What is the secondary dew point? Is there also a secondary bubble point?

## EXERCISES

## Section 4.1

## 4.1. Degrees-of-freedom for a three-phase equilibrium.

Consider the equilibrium stage shown in Figure 4.34. Conduct a degrees-of-freedom analysis by performing the following steps: (a) list and count the variables; (b) write and count the equations relating the variables; (c) calculate the degrees of freedom; and (d) list a reasonable set of design variables.

## 4.2. Uniqueness of three different separation operations.

Can the following problems be solved uniquely?

- (a) The feed streams to an adiabatic equilibrium stage consist of liquid and vapor streams of known composition, flow rate,

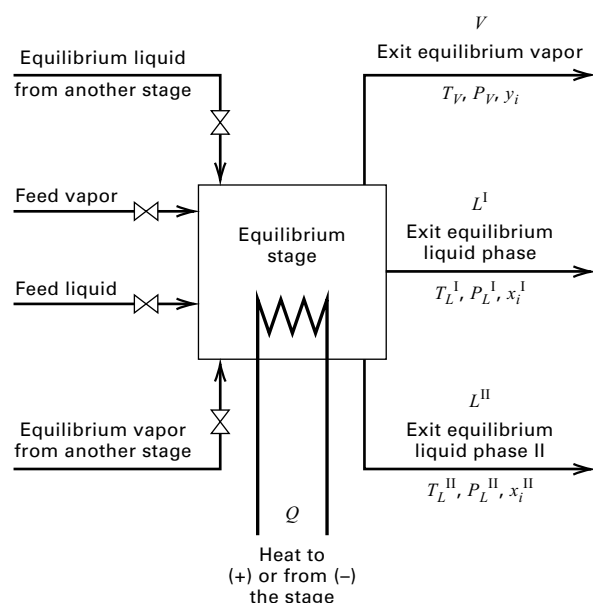


Figure 4.34 Conditions for Exercise 4.1.

temperature, and pressure. Given the stage (outlet) temperature and pressure, calculate the composition and amounts of equilibrium vapor and liquid leaving.

- (b) The same as part (a), except that the stage is not adiabatic.
- (c) A vapor of known  $T$ ,  $P$ , and composition is partially condensed. The outlet  $P$  of the condenser and the inlet cooling water  $T$  are fixed. Calculate the cooling water required.

## 4.3. Degrees-of-freedom for an adiabatic, two-phase flash.

Consider an adiabatic equilibrium flash. The variables are all as indicated in Figure 4.10a with  $Q = 0$ . (a) Determine the number of variables. (b) Write all the independent equations that relate the variables. (c) Determine the number of equations. (d) Determine the number of degrees of freedom. (e) What variables would you prefer to specify in order to solve an adiabatic-flash problem?

## 4.4. Degrees of freedom for a nonadiabatic, three-phase flash.

Determine the number of degrees of freedom for a nonadiabatic equilibrium flash for the liquid feed and three products shown in Figure 4.32.

## 4.5. Application of Gibbs phase rule.

For the seven-phase equilibrium system shown in Figure 4.30, assume air consists of  $N_2$ ,  $O_2$ , and argon. What is the number of degrees of freedom? What variables might be specified?

## Section 4.2

## 4.6. Partial vaporization of a nonideal binary mixture.

A liquid mixture containing 25 mol% benzene and 75 mol% ethyl alcohol, in which components are miscible in all proportions, is heated at a constant pressure of 1 atm from 60°C to 90°C. Using the following  $T$ - $x$ - $y$  experimental data, determine (a) the temperature where vaporization begins; (b) the composition of the first bubble of vapor; (c) the composition of the residual liquid when 25 mol% has evaporated, assuming that all vapor formed is retained in the apparatus and is in equilibrium with the residual liquid. (d) Repeat

part (c) for 90 mol% vaporized. (e) Repeat part (d) if, after 25 mol% is vaporized as in part (c), the vapor formed is removed and an additional 35 mol% is vaporized by the same technique used in part (c). (f) Plot temperature versus mol% vaporized for parts (c) and (e).

#### $T$ - $x$ - $y$ DATA FOR BENZENE-ETHYL ALCOHOL AT 1 ATM

| Temperature, °C:                |      |    |      |    |      |      |      |      |    |      |      |
|---------------------------------|------|----|------|----|------|------|------|------|----|------|------|
| 78.4                            | 77.5 | 75 | 72.5 | 70 | 68.5 | 67.7 | 68.5 | 72.5 | 75 | 77.5 | 80.1 |
| Mole percent benzene in vapor:  |      |    |      |    |      |      |      |      |    |      |      |
| 0                               | 7.5  | 28 | 42   | 54 | 60   | 68   | 73   | 82   | 88 | 95   | 100  |
| Mole percent benzene in liquid: |      |    |      |    |      |      |      |      |    |      |      |
| 0                               | 1.5  | 5  | 12   | 22 | 31   | 68   | 81   | 91   | 95 | 98   | 100  |

(g) Use the following vapor pressure data with Raoult's and Dalton's laws to construct a  $T$ - $x$ - $y$  diagram, and compare it to the answers obtained in parts (a) and (f) with those obtained using the experimental  $T$ - $x$ - $y$  data. What are your conclusions?

#### VAPOR PRESSURE DATA

| Vapor pressure, torr: |      |      |      |      |      |      |
|-----------------------|------|------|------|------|------|------|
| 20                    | 40   | 60   | 100  | 200  | 400  | 760  |
| Ethanol, °C:          |      |      |      |      |      |      |
| 8                     | 19.0 | 26.0 | 34.9 | 48.4 | 63.5 | 78.4 |
| Benzene, °C:          |      |      |      |      |      |      |
| -2.6                  | 7.6  | 15.4 | 26.1 | 42.2 | 60.6 | 80.1 |

#### 4.7. Steam distillation of stearic acid.

Stearic acid is steam distilled at 200°C in a direct-fired still. Steam is introduced into the molten acid in small bubbles, and the acid in the vapor leaving the still has a partial pressure equal to 70% of the vapor pressure of pure stearic acid at 200°C. Plot the kg acid distilled per kg steam added as a function of total pressure from 101.3 kPa to 3.3 kPa at 200°C. The vapor pressure of stearic acid at 200°C is 0.40 kPa.

#### 4.8. Equilibrium plots for benzene-toluene.

The relative volatility,  $\alpha$ , of benzene to toluene at 1 atm is 2.5. Construct  $x$ - $y$  and  $T$ - $x$ - $y$  diagrams for this system at 1 atm. Repeat the construction of the  $x$ - $y$  diagram using vapor pressure data for benzene from Exercise 4.6 and for toluene from the table below, with Raoult's and Dalton's laws. Use the diagrams for the following: (a) A liquid containing 70 mol% benzene and 30 mol% toluene is heated in a container at 1 atm until 25 mol% of the original liquid is evaporated. Determine the temperature. The phases are then separated mechanically, and the vapors condensed. Determine the composition of the condensed vapor and the liquid residue. (b) Calculate and plot the  $K$ -values as a function of temperature at 1 atm.

#### VAPOR PRESSURE OF TOLUENE

| Vapor pressure, torr: |      |      |      |      |      |       |       |
|-----------------------|------|------|------|------|------|-------|-------|
| 20                    | 40   | 60   | 100  | 200  | 400  | 760   | 1,520 |
| Temperature, °C:      |      |      |      |      |      |       |       |
| 18.4                  | 31.8 | 40.3 | 51.9 | 69.5 | 89.5 | 110.6 | 136   |

#### 4.9. Vapor-liquid equilibrium for heptane-toluene system.

(a) The vapor pressure of toluene is given in Exercise 4.8, and that of  $n$ -heptane is in the table below. Construct the following plots:

(a) an  $x$ - $y$  diagram at 1 atm using Raoult's and Dalton's laws; (b) a  $T$ - $x$  bubble-point curve at 1 atm; (c)  $\alpha$  and  $K$ -values versus temperature; and (d) repeat of part (a) using an average value of  $\alpha$ . Then, (e) compare your  $x$ - $y$  and  $T$ - $x$ - $y$  diagrams with the following experimental data of Steinhauser and White [*Ind. Eng. Chem.*, **41**, 2912 (1949)].

#### VAPOR PRESSURE OF $n$ -HEPTANE

| Vapor pressure, torr: |      |      |      |      |      |      |       |
|-----------------------|------|------|------|------|------|------|-------|
| 20                    | 40   | 60   | 100  | 200  | 400  | 760  | 1,520 |
| Temperature, °C:      |      |      |      |      |      |      |       |
| 9.5                   | 22.3 | 30.6 | 41.8 | 58.7 | 78.0 | 98.4 | 124   |

#### VAPOR-LIQUID EQUILIBRIUM DATA FOR $n$ -HEPTANE/TOLUENE AT 1 ATM

| $x_{n\text{-heptane}}$ | $y_{n\text{-heptane}}$ | $T, ^\circ\text{C}$ |
|------------------------|------------------------|---------------------|
| 0.025                  | 0.048                  | 110.75              |
| 0.129                  | 0.205                  | 106.80              |
| 0.354                  | 0.454                  | 102.95              |
| 0.497                  | 0.577                  | 101.35              |
| 0.843                  | 0.864                  | 98.90               |
| 0.940                  | 0.948                  | 98.50               |
| 0.994                  | 0.993                  | 98.35               |

#### 4.10. Continuous, single-stage distillation.

Saturated-liquid feed of  $F = 40$  mol/h, containing 50 mol% A and B, is supplied to the apparatus in Figure 4.35. The condensate is split so that reflux/condensate = 1.

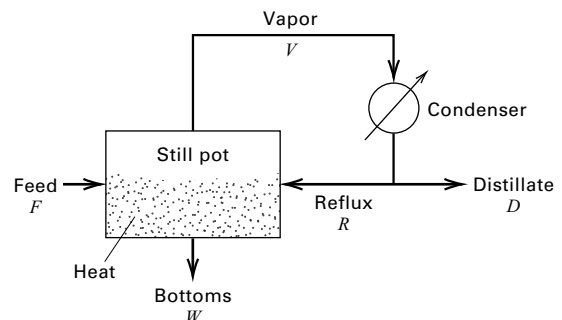


Figure 4.35 Conditions for Exercise 4.10.

(a) If heat is supplied such that  $W = 30$  mol/h and  $\alpha = 2$ , as defined below, what will be the composition of the overhead and the bottoms product?

$$\alpha = \frac{P_A^s}{P_B^s} = \frac{y_A x_B}{y_B x_A}$$

(b) If the operation is changed so that no condensate is returned to the still pot and  $W = 3D$ , compute the product compositions.

#### 4.11. Partial vaporization of feed to a distillation column.

A fractionation tower operating at 101.3 kPa produces a distillate of 95 mol% acetone (A), 5 mol% water, and a residue containing 1 mol% A. The feed liquid is at 125°C and 687 kPa and contains 57 mol% A. Before entering the tower, the feed passes through an expansion valve and is partially vaporized at 60°C. From the data

below, determine the molar ratio of liquid to vapor in the feed. Enthalpy and equilibrium data are: molar latent heat of A = 29,750 kJ/kmol; molar latent heat of H<sub>2</sub>O = 42,430 kJ/kmol; molar specific heat of A = 134 kJ/kmol-K; molar specific heat of H<sub>2</sub>O = 75.3 kJ/kmol-K; enthalpy of high-pressure, hot feed before adiabatic expansion = 0; enthalpies of feed phases after expansion are  $h_V = 27,200$  kJ/kmol and  $h_L = -5,270$  kJ/kmol. All data except  $K$ -values, are temperature-independent.

#### EQUILIBRIUM DATA FOR ACETONE–H<sub>2</sub>O AT 101.3 kPa

|                       | T, °C |      |      |      |      |      |     |
|-----------------------|-------|------|------|------|------|------|-----|
|                       | 56.7  | 57.1 | 60.0 | 61.0 | 63.0 | 71.7 | 100 |
| Mol% A in liquid: 100 | 92.0  | 50.0 | 33.0 | 17.6 | 6.8  | 0    |     |
| Mol% A in vapor: 100  | 94.4  | 85.0 | 83.7 | 80.5 | 69.2 | 0    |     |

#### 4.12. Enthalpy-concentration diagram.

Using vapor pressure data from Exercises 4.6 and 4.8 and the enthalpy data provided below: (a) construct an  $h$ - $x$ - $y$  diagram for the benzene–toluene system at 1 atm (101.3 kPa) based on Raoult's and Dalton's laws, and (b) calculate the energy required for 50 mol% vaporization of a 30 mol% liquid solution of benzene in toluene at saturation temperature. If the vapor is condensed, what is the heat load on the condenser in kJ/kg of solution if the condensate is saturated, and if it is subcooled by 10°C?

| T, °C | Saturated Enthalpy, kJ/kg |       |         |       |
|-------|---------------------------|-------|---------|-------|
|       | Benzene                   |       | Toluene |       |
|       | $h_L$                     | $h_V$ | $h_L$   | $h_V$ |
| 60    | 79                        | 487   | 77      | 471   |
| 80    | 116                       | 511   | 114     | 495   |
| 100   | 153                       | 537   | 151     | 521   |

#### Section 4.3

#### 4.13. Azeotrope of chloroform–methanol.

Vapor–liquid equilibrium data at 101.3 kPa are given for the chloroform–methanol system on p. 13-11 of *Perry's Chemical Engineers' Handbook*, 6th ed. From these data, prepare plots like Figures 4.6b and 4.6c. From the plots, determine the azeotropic composition, type of azeotrope, and temperature at 101.3 kPa.

#### 4.14. Azeotrope of water–formic acid.

Vapor–liquid equilibrium data at 101.3 kPa are given for the water–formic acid system on p. 13-14 of *Perry's Chemical Engineers' Handbook*, 6th ed. From these data, prepare plots like Figures 4.7b and 4.7c. From the plots, determine the azeotropic composition, type of azeotrope, and temperature at 101.3 kPa.

#### 4.15. Partial vaporization of water–isopropanol mixture.

Vapor–liquid equilibrium data for mixtures of water and isopropanol at 1 atm are given below. (a) Prepare  $T$ - $x$ - $y$  and  $x$ - $y$  diagrams. (b) When a solution containing 40 mol% isopropanol is slowly vaporized, what is the composition of the initial vapor? (c) If the mixture in part (b) is heated until 75 mol% is vaporized, what are the compositions of the equilibrium vapor and liquid? (d) Calculate  $K$ -values and values of  $\alpha$  at 80°C and 89°C. (e) Compare your answers in parts (a), (b), and (c) to those obtained from  $T$ - $x$ - $y$  and  $x$ - $y$  diagrams based on the following vapor pressure data and Raoult's and Dalton's laws. What do you conclude?

#### VAPOR–LIQUID EQUILIBRIUM DATA FOR ISOPROPANOL AND WATER AT 1 ATM

| T, °C | Mol% Isopropanol |       |
|-------|------------------|-------|
|       | Liquid           | Vapor |
| 93.00 | 1.18             | 21.95 |
| 84.02 | 8.41             | 46.20 |
| 83.85 | 9.10             | 47.06 |
| 81.64 | 28.68            | 53.44 |
| 81.25 | 34.96            | 55.16 |
| 80.32 | 60.30            | 64.22 |
| 80.16 | 67.94            | 68.21 |
| 80.21 | 68.10            | 68.26 |
| 80.28 | 76.93            | 74.21 |
| 80.66 | 85.67            | 82.70 |
| 81.51 | 94.42            | 91.60 |

Notes: Composition of the azeotrope:  $x = y = 68.54\%$ .

Boiling point of azeotrope: 80.22°C.

Boiling point of pure isopropanol: 82.5°C.

#### Vapor Pressures of Isopropanol and Water

|                      | 200  | 400  | 760  |
|----------------------|------|------|------|
| Vapor pressure, torr |      |      |      |
| Isopropanol, °C      | 53.0 | 67.8 | 82.5 |
| Water, °C            | 66.5 | 83   | 100  |

#### Section 4.4

#### 4.16. Vaporization of mixtures of hexane and octane.

Using the  $y$ - $x$  and  $T$ - $y$ - $x$  diagrams in Figures 4.3 and 4.4, determine the temperature, amounts, and compositions of the vapor and liquid phases at 101 kPa for the following conditions with a 100-kmol mixture of  $nC_6$  (H) and  $nC_8$  (C). (a)  $z_H = 0.5$ ,  $\Psi = V/F = 0.2$ ; (b)  $z_H = 0.4$ ,  $y_H = 0.6$ ; (c)  $z_H = 0.6$ ,  $x_C = 0.7$ ; (d)  $z_H = 0.5$ ,  $\Psi = 0$ ; (e)  $z_H = 0.5$ ,  $\Psi = 1.0$ ; and (f)  $z_H = 0.5$ ,  $T = 200^\circ\text{F}$

#### 4.17. Derivation of equilibrium-flash equations for a binary mixture.

For a binary mixture of components 1 and 2, show that the phase compositions and amounts can be computed directly from the following reduced forms of Eqs. (5), (6), and (3) of Table 4.4:

$$\begin{aligned}x_1 &= (1 - K_2)/(K_1 - K_2) \\x_2 &= 1 - x_1 \\y_1 &= (K_1 K_2 - K_1)/(K_2 - K_1) \\y_2 &= 1 - y_1 \\ \Psi &= \frac{V}{F} = \frac{z_1[(K_1 - K_2)/(1 - K_2)] - 1}{K_1 - 1}\end{aligned}$$

#### 4.18. Conditions for Rachford–Rice equation to be satisfied.

Consider the Rachford–Rice form of the flash equation,

$$\sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + (V/F)(K_i - 1)} = 0$$

Under what conditions can this equation be satisfied?

#### 4.19. Equilibrium flash using a graph.

A liquid containing 60 mol% toluene and 40 mol% benzene is continuously distilled in a single equilibrium stage at 1 atm. What percent of benzene in the feed leaves as vapor if 90% of the toluene entering in the feed leaves as liquid? Assume a relative volatility of 2.3 and obtain the solution graphically.

**4.20. Flash vaporization of a benzene–toluene mixture.**

Solve Exercise 4.19 by assuming an ideal solution with vapor pressure data from Figure 2.3. Also determine the temperature.

**4.21. Equilibrium flash of seven-component mixture.**

A seven-component mixture is flashed at a fixed  $P$  and  $T$ . (a) Using the  $K$ -values and feed composition below, make a plot of the Rachford–Rice flash function

$$f\{\Psi\} = \sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)}$$

at intervals of  $\Psi$  of 0.1, and estimate the correct root of  $\Psi$ .

(b) An alternative form of the flash function is

$$f\{\Psi\} = \sum_{i=1}^C \frac{z_i K_i}{1 + \Psi(K_i - 1)} - 1$$

Make a plot of this equation at intervals of  $\Psi$  of 0.1 and explain why the Rachford–Rice function is preferred.

| Component | $z_i$  | $K_i$ |
|-----------|--------|-------|
| 1         | 0.0079 | 16.2  |
| 2         | 0.1321 | 5.2   |
| 3         | 0.0849 | 2.6   |
| 4         | 0.2690 | 1.98  |
| 5         | 0.0589 | 0.91  |
| 6         | 0.1321 | 0.72  |
| 7         | 0.3151 | 0.28  |

**4.22. Equilibrium flash of a hydrocarbon mixture.**

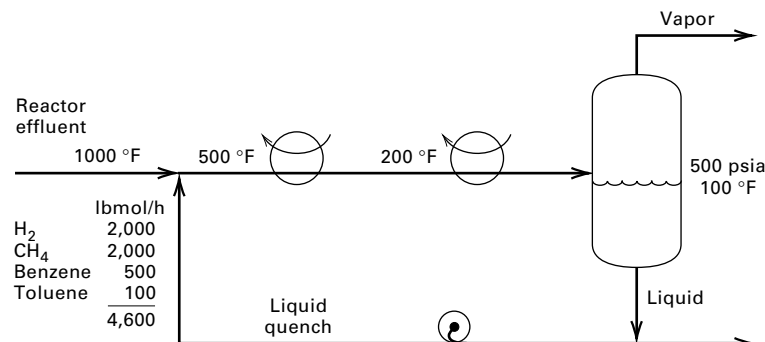
One hundred kmol of a feed composed of 25 mol%  $n$ -butane, 40 mol%  $n$ -pentane, and 35 mol%  $n$ -hexane is flashed. If 80% of the hexane is in the liquid at 240°F, what are the pressure and the liquid and vapor compositions? Obtain  $K$ -values from Figure 2.4.

**4.23. Equilibrium-flash vaporization of a hydrocarbon mixture.**

An equimolar mixture of ethane, propane,  $n$ -butane, and  $n$ -pentane is subjected to flash vaporization at 150°F and 205 psia. What are the expected amounts and compositions of the products? Is it possible to recover 70% of the ethane in the vapor by a single-stage flash at other conditions without losing more than 5% of  $nC_4$  to the vapor? Obtain  $K$ -values from Figure 2.4.

**4.24. Cooling of a reactor effluent with recycled liquid.**

Figure 4.36 shows a system to cool reactor effluent and separate light gases from hydrocarbons.  $K$ -values at 500 psia and 100°F are:



| Component       | $K_i$ |
|-----------------|-------|
| H <sub>2</sub>  | 80    |
| CH <sub>4</sub> | 10    |
| Benzene         | 0.010 |
| Toluene         | 0.004 |

(a) Calculate composition and flow rate of vapor leaving the flash drum. (b) Does the liquid-quench flow rate influence the result? Prove your answer analytically.

**4.25. Partial condensation of a gas mixture.**

The feed in Figure 4.37 is partially condensed. Calculate the amounts and compositions of the equilibrium phases,  $V$  and  $L$ .

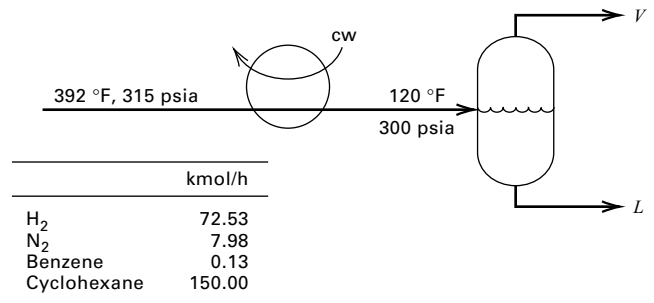


Figure 4.37 Conditions for Exercise 4.25.

**4.26. Rapid determination of phase condition.**

The following stream is at 200 psia and 200°F. Without making a flash calculation, determine if it is a subcooled liquid or a superheated vapor, or if it is partially vaporized.

| Component      | lbmol/h | $K$ -value |
|----------------|---------|------------|
| C <sub>3</sub> | 125     | 2.056      |
| $nC_4$         | 200     | 0.925      |
| $nC_5$         | 175     | 0.520      |

**4.27. Determination of reflux-drum pressure.**

Figure 4.38 shows the overhead system for a distillation column. The composition of the total distillates is indicated, with 10 mol% being vapor. Determine reflux-drum pressure if the temperature is 100°F. Use the  $K$ -values below, assuming that  $K$  is inversely proportional to pressure.

Figure 4.36 Conditions for Exercise 4.24.

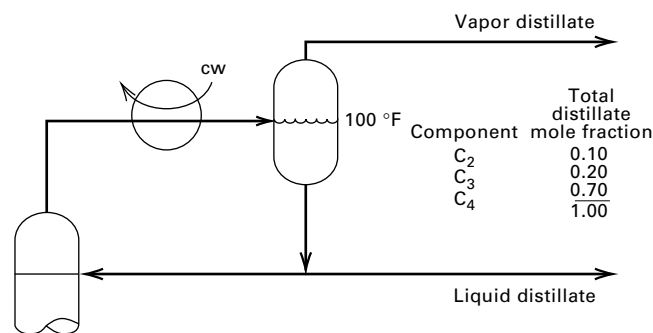


Figure 4.38 Conditions for Exercise 4.27.

| Component      | $K$ at 100°F, 200 psia |
|----------------|------------------------|
| C <sub>2</sub> | 2.7                    |
| C <sub>3</sub> | 0.95                   |
| C <sub>4</sub> | 0.34                   |

#### 4.28. Flash calculations for different $K$ -value correlations.

Determine the phase condition of a stream having the following composition at 7.2°C and 2,620 kPa.

| Component          | kmol/h |
|--------------------|--------|
| N <sub>2</sub>     | 1.0    |
| C <sub>1</sub>     | 124.0  |
| C <sub>2</sub>     | 87.6   |
| C <sub>3</sub>     | 161.6  |
| $n$ C <sub>4</sub> | 176.2  |
| $n$ C <sub>5</sub> | 58.5   |
| $n$ C <sub>6</sub> | 33.7   |

Use a process simulator with the S–R–K and P–R options for  $K$ -values, together with one other option, e.g., B–W–R–S. Does the choice of  $K$ -value method influence the results significantly?

#### 4.29. Flash calculations at different values of $T$ and $P$ .

A liquid mixture consisting of 100 kmol of 60 mol% benzene, 25 mol% toluene, and 15 mol% *o*-xylene is flashed at 1 atm and 100°C. Assuming ideal solutions, use vapor pressure data from a process simulator to: (a) Compute kmol amounts and mole-fraction compositions of liquid and vapor products. (b) Repeat the calculation at 100°C and 2 atm. (c) Repeat the calculation at 105°C and 0.1 atm. (d) Repeat the calculation at 150°C and 1 atm.

#### 4.30. Conditions at vapor–liquid equilibrium.

Using equations in Table 4.4, prove that the vapor leaving an equilibrium flash is at its dew point and that the liquid leaving is at its bubble point.

#### 4.31. Bubble-point temperature of feed to a distillation column.

The feed below enters a distillation column as saturated liquid at 1.72 MPa. Calculate the bubble-point temperature using the  $K$ -values of Figure 2.4.

| Compound          | kmol/h |
|-------------------|--------|
| Ethane            | 1.5    |
| Propane           | 10.0   |
| <i>n</i> -Butane  | 18.5   |
| <i>n</i> -Pentane | 17.5   |
| <i>n</i> -Hexane  | 3.5    |

#### 4.32. Bubble- and dew-point pressures of a binary mixture.

An equimolar solution of benzene and toluene is evaporated at a constant temperature of 90°C. What are the pressures at the beginning and end of the vaporization? Assume an ideal solution and use the vapor pressure curves of Figure 2.3, or use a process simulator.

#### 4.33. Bubble point, dew point, and flash of a water–acetic acid mixture.

The following equations are given by Sebastiani and Lacquaniti [*Chem. Eng. Sci.*, **22**, 1155 (1967)] for the liquid-phase activity coefficients of the water (W)–acetic acid (A) system.

$$\log \gamma_W = x_A^2 [A + B(4x_W - 1) + C(x_W - x_A)(6x_W - 1)]$$

$$\log \gamma_A = x_W^2 [A + B(4x_W - 3) + C(x_W - x_A)(6x_W - 5)]$$

$$A = 0.1182 + \frac{64.24}{T(\text{K})}$$

$$B = 0.1735 - \frac{43.27}{T(\text{K})}$$

$$C = 0.1081$$

Find the dew point and bubble point of the mixture  $x_W = 0.5$ ,  $x_A = 0.5$ , at 1 atm. Flash the mixture at a temperature halfway between the dew and bubble points.

#### 4.34. Bubble point, dew point, and flash of a mixture.

Find the bubble point and dew point of a mixture of 0.4 mole fraction toluene (1) and 0.6 mole fraction *n*-butanol (2) at 101.3 kPa.  $K$ -values can be calculated from (2-72) using vapor-pressure data, and  $\gamma_1$  and  $\gamma_2$  from the van Laar equation of Table 2.9 with  $A_{12} = 0.855$  and  $A_{21} = 1.306$ . If the same mixture is flashed midway between the bubble and dew points and 101.3 kPa, what fraction is vaporized, and what are the phase compositions?

#### 4.35. Bubble point, dew point, and azeotrope of mixture.

For a solution of a molar composition of ethyl acetate (A) of 80% and ethyl alcohol (E) of 20%: (a) Calculate the bubble-point temperature at 101.3 kPa and the composition of the corresponding vapor using (2-72) with vapor pressure data and the van Laar equation of Table 2.9 with  $A_{AE} = 0.855$ ,  $A_{EA} = 0.753$ . (b) Find the dew point of the mixture. (c) Does the mixture form an azeotrope? If so, predict the temperature and composition.

#### 4.36. Bubble point, dew point, and azeotrope of a mixture.

A solution at 107°C contains 50 mol% water (W) and 50 mol% formic acid (F). Using (2-72) with vapor pressure data and the van Laar equation with  $A_{WF} = -0.2935$  and  $A_{FW} = -0.2757$ : (a) Compute the bubble-point pressure. (b) Compute the dew-point pressure. (c) Determine if the mixture forms an azeotrope. If so, predict the azeotropic pressure at 107°C and the composition.

#### 4.37. Bubble point, dew point, and equilibrium flash of a ternary mixture.

For a mixture of 45 mol% *n*-hexane, 25 mol% *n*-heptane, and 30 mol% *n*-octane at 1 atm, use a process simulator to: (a) Find the bubble- and dew-point temperatures. (b) Find the flash temperature, compositions, and relative amounts of liquid and vapor products if the mixture is subjected to a flash distillation at 1 atm so that 50 mol % is vaporized. (c) Find how much octane is taken off as vapor if 90% of the hexane is taken off as vapor. (d) Repeat parts (a) and (b) at 5 atm and 0.5 atm.

#### 4.38. Vaporization of column bottoms in a partial reboiler.

In Figure 4.39, 150 kmol/h of a saturated liquid,  $L_1$ , at 758 kPa of molar composition propane 10%, *n*-butane 40%, and *n*-pentane 50% enters the reboiler from stage 1. Use a process simulator to find the compositions and amounts of  $V_B$  and  $B$ . What is  $Q_R$ , the reboiler duty?

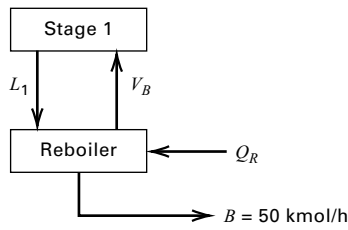


Figure 4.39 Conditions for Exercise 4.38.

**4.39. Bubble point and flash temperatures for a ternary mixture.**

For a mixture with mole fractions 0.005 methane, 0.595 ethane, and the balance *n*-butane at 50 psia, and using *K*-values from Figure 2.4: (a) Find the bubble-point temperature. (b) Find the temperature that results in 25% vaporization at this pressure, and determine the liquid and vapor compositions in mole fractions.

**4.40. Heating and expansion of a hydrocarbon mixture.**

In Figure 4.40, a mixture is heated and expanded before entering a distillation column. Calculate, using a process simulator, mole percent vapor and vapor and liquid mole fractions at locations indicated by pressure specifications.

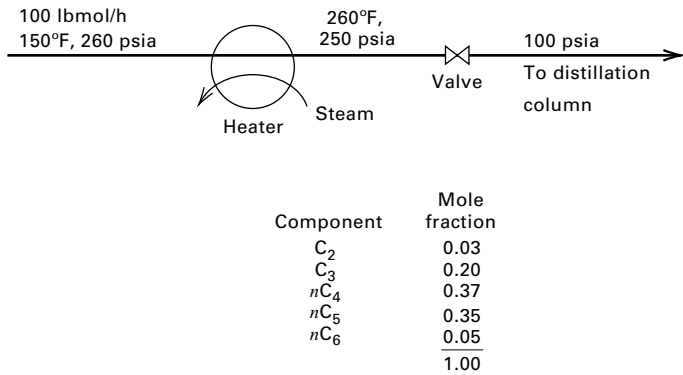


Figure 4.40 Conditions for Exercise 4.40.

**4.41. Equilibrium vapor and liquid leaving a feed stage.**

Streams entering stage *F* of a distillation column are shown in Figure 4.41. Using a process simulator, find the stage temperature and compositions and amounts of streams *V<sub>F</sub>* and *L<sub>F</sub>* if the pressure is 785 kPa.

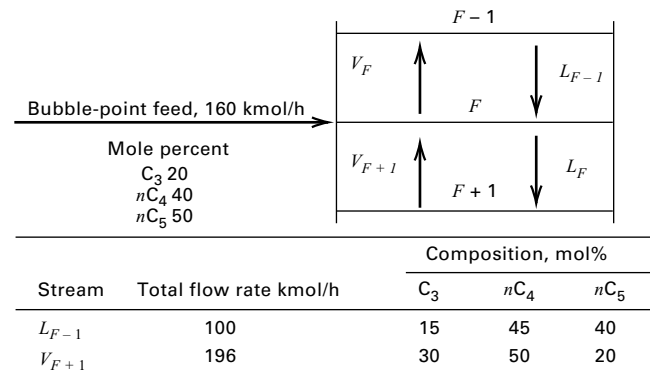


Figure 4.41 Conditions for Exercise 4.41.

**4.42. Adiabatic flash across a valve.**

The stream below is flashed adiabatically across a valve. Conditions upstream are 250°F and 500 psia, and downstream are 300

psia. Compute using a process simulator the: (a) phase condition upstream of the valve; (b) temperature downstream of the valve; (c) molar fraction vaporized downstream of the valve; and (d) mole-fraction compositions of the vapor and liquid phases downstream of the valve.

| Component                     | <i>z<sub>i</sub></i> |
|-------------------------------|----------------------|
| C <sub>2</sub> H <sub>4</sub> | 0.02                 |
| C <sub>2</sub> H <sub>6</sub> | 0.03                 |
| C <sub>3</sub> H <sub>6</sub> | 0.05                 |
| C <sub>3</sub> H <sub>8</sub> | 0.10                 |
| <i>i</i> C <sub>4</sub>       | 0.20                 |
| <i>n</i> C <sub>4</sub>       | 0.60                 |

**4.43. Single-stage equilibrium flash of a clarified broth.**

The ABE biochemical process makes acetone, *n*-butanol, and ethanol by an anaerobic, submerged, batch fermentation at 30°C of corn kernels, using a strain of the bacterium *Clostridia acetobutylicum*. Following fermentation, the broth is separated from the biomass solids by centrifugation. Consider 1,838,600 L/h of clarified broth of S.G. = 0.994, with a titer of 22.93 g/L of ABE in the mass ratio of 3.0:7.5:1.0. A number of continuous bioseparation schemes have been proposed, analyzed, and applied. In particular, the selection of the first separation step needs much study because the broth is so dilute in the bioproducts. Possibilities are single-stage flash, distillation, liquid-liquid extraction, and pervaporation. In this exercise, a single-stage flash is to be investigated. Convert the above data on the clarified broth to component flow rates in kmol/h. Heat the stream to 97°C at 101.3 kPa. Use a process simulator to run a series of equilibrium-flash calculations using the NRTL equation for liquid-phase activity coefficients. Note that *n*-butanol and ethanol both form an azeotrope with water. Also, *n*-butanol may not be completely soluble in water for all concentrations. The specifications for each flash calculation are pressure = 101.3 kPa and *V/F*, the molar vapor-to-feed ratio. A *V/F* is to be sought that maximizes the ABE in the vapor while minimizing the water in the vapor. Because the boiling point of *n*-butanol is greater than that of water, and because of possible azeotrope formation and other nonideal solution effects, a suitable *V/F* may not exist.

**4.44. Algorithms for various flash calculations.**

Given the isothermal-flash algorithm and Table 4.4, propose algorithms for the following flash calculations, assuming that expressions for *K*-values and enthalpies are available.

| Given                           | Find                            |
|---------------------------------|---------------------------------|
| <i>h<sub>F</sub></i> , <i>P</i> | $\Psi$ , <i>T</i>               |
| <i>h<sub>F</sub></i> , <i>T</i> | $\Psi$ , <i>P</i>               |
| <i>h<sub>F</sub></i> , $\Psi$   | <i>T</i> , <i>P</i>             |
| $\Psi$ , <i>T</i>               | <i>h<sub>F</sub></i> , <i>P</i> |
| $\Psi$ , <i>P</i>               | <i>h<sub>F</sub></i> , <i>T</i> |
| <i>T</i> , <i>P</i>             | <i>h<sub>F</sub></i> , $\Psi$   |

**Section 4.5**

**4.45. Comparison of solvents for single-stage extraction.**

A feed of 13,500 kg/h is 8 wt% acetic acid (B) in water (A). Removal of acetic acid is to be by liquid-liquid extraction at 25°C. The raffinate is to contain 1 wt% acetic acid. The following four

solvents, with accompanying distribution (partition) coefficients in mass-fraction units, are candidates. Water and each solvent (C) can be considered immiscible. For each solvent, estimate the kg/hr required if one equilibrium stage is used.

| Solvent         | $K_D$ |
|-----------------|-------|
| Methyl acetate  | 1.273 |
| Isopropyl ether | 0.429 |
| Heptadecanol    | 0.312 |
| Chloroform      | 0.178 |

#### 4.46. Liquid–liquid extraction of ethylene glycol from water by furfural.

Forty-five kg of a solution of 30 wt% ethylene glycol in water is to be extracted with furfural. Using Figures 4.14a and 4.14c, calculate the: (a) minimum kg of solvent; (b) maximum kg of solvent; (c) kg of solvent-free extract and raffinate for 45 kg solvent, and the percentage glycol extracted; and (d) maximum purity of glycol in the extract and the maximum purity of water in the raffinate for one stage.

#### 4.47. Representation of a ternary on a triangular diagram.

Prove that, in a triangular diagram where each vertex represents a pure component, the composition of the system at any point inside the triangle is proportional to the length of the respective perpendicular drawn from the point to the side of the triangle opposite the vertex in question. Note that it is not necessary that the triangle be of a right or equilateral type.

#### 4.48. Liquid–liquid extraction of acetic acid from chloroform by water.

A mixture of chloroform ( $\text{CHCl}_3$ ) and acetic acid at 18°C and 1 atm (101.3 kPa) is extracted with water to recover the acid. Forty-five kg of 35 wt%  $\text{CHCl}_3$  and 65 wt% acid is treated with 22.75 kg of water at 18°C in a one-stage batch extraction. (a) What are the compositions and masses of the raffinate and extract layers? (b) If the raffinate layer from part (a) is extracted again with one-half its weight of water, what are the compositions and weights of the new layers? (c) If all the water is removed from the final raffinate layer of part (b), what will its composition be? Solve this exercise using the following equilibrium data to construct one or more of the types of diagrams in Figure 4.13.

#### LIQUID–LIQUID EQUILIBRIUM DATA FOR $\text{CHCl}_3$ – $\text{H}_2\text{O}$ – $\text{CH}_3\text{COOH}$ AT 18°C AND 1 ATM

| Heavy Phase (wt%) |                      |                          | Light Phase (wt%) |                      |                          |
|-------------------|----------------------|--------------------------|-------------------|----------------------|--------------------------|
| $\text{CHCl}_3$   | $\text{H}_2\text{O}$ | $\text{CH}_3\text{COOH}$ | $\text{CHCl}_3$   | $\text{H}_2\text{O}$ | $\text{CH}_3\text{COOH}$ |
| 99.01             | 0.99                 | 0.00                     | 0.84              | 99.16                | 0.00                     |
| 91.85             | 1.38                 | 6.77                     | 1.21              | 73.69                | 25.10                    |
| 80.00             | 2.28                 | 17.72                    | 7.30              | 48.58                | 44.12                    |
| 70.13             | 4.12                 | 25.75                    | 15.11             | 34.71                | 50.18                    |
| 67.15             | 5.20                 | 27.65                    | 18.33             | 31.11                | 50.56                    |
| 59.99             | 7.93                 | 32.08                    | 25.20             | 25.39                | 49.41                    |
| 55.81             | 9.58                 | 34.61                    | 28.85             | 23.28                | 47.87                    |

#### 4.49.

Isopropyl ether (E) is used to separate acetic acid (A) from water (W). The liquid–liquid equilibrium data at 25°C and 1 atm are below: (a) One hundred kilograms of a 30 wt% A–W solution is contacted

with 120 kg of ether (E). What are the compositions and weights of the resulting extract and raffinate? What would the concentration of acid in the (ether-rich) extract be if all ether were removed? (b) A solution of 52 kg A and 48 kg W is contacted with 40 kg of E. Calculate the extract and raffinate compositions and quantities.

#### LIQUID–LIQUID EQUILIBRIUM DATA FOR ACETIC ACID (A), WATER (W), AND ISOPROPANOL ETHER (E) AT 25°C AND 1 ATM

| Water-Rich Layer |       |       | Ether-Rich Layer |       |       |
|------------------|-------|-------|------------------|-------|-------|
| Wt% A            | Wt% W | Wt% E | Wt% A            | Wt% W | Wt% E |
| 1.41             | 97.1  | 1.49  | 0.37             | 0.73  | 98.9  |
| 2.89             | 95.5  | 1.61  | 0.79             | 0.81  | 98.4  |
| 6.42             | 91.7  | 1.88  | 1.93             | 0.97  | 97.1  |
| 13.30            | 84.4  | 2.3   | 4.82             | 1.88  | 93.3  |
| 25.50            | 71.1  | 3.4   | 11.4             | 3.9   | 84.7  |
| 36.70            | 58.9  | 4.4   | 21.6             | 6.9   | 71.5  |
| 45.30            | 45.1  | 9.6   | 31.1             | 10.8  | 58.1  |
| 46.40            | 37.1  | 16.5  | 36.2             | 15.1  | 48.7  |

#### Section 4.6

#### 4.50. Separation of paraffins from aromatics by liquid–liquid extraction.

Diethylene glycol (DEG) is the solvent in the UDEX liquid–liquid extraction process [H.W. Grote, *Chem. Eng. Progr.*, **54**(8), 43 (1958)] to separate paraffins from aromatics. If 280 lbmol/h of 42.86 mol% *n*-hexane, 28.57 mol% *n*-heptane, 17.86 mol% benzene, and 10.71 mol% toluene is contacted with 500 lbmol/h of 90 mol% aqueous DEG at 325°F and 300 psia, calculate, using a process simulator with the UNIFAC L/L method for liquid-phase activity coefficients, the flow rates and molar compositions of the resulting two liquid phases. Is DEG more selective for the paraffins or the aromatics?

#### 4.51. Liquid–liquid extraction of organic acids from water with ethyl acetate.

A feed of 110 lbmol/h includes 5, 3, and 2 lbmol/h, respectively, of formic, acetic, and propionic acids in water. If the acids are extracted in one equilibrium stage with 100 lbmol/h of ethyl acetate (EA), calculate, with a process simulator using the UNIFAC method, the flow rates and compositions of the resulting liquid phases. What is the selectivity of EA for the organic acids?

#### Section 4.7

#### 4.52. Leaching of oil from soybean flakes by a hexane.

Repeat Example 4.9 for 200,000 kg/h of hexane.

#### 4.53. Leaching of $\text{Na}_2\text{CO}_3$ from a solid by water.

Water is used in an equilibrium stage to dissolve 1,350 kg/h of  $\text{Na}_2\text{CO}_3$  from 3,750 kg/h of a solid, where the balance is an insoluble oxide. If 4,000 kg/h of water is used and the underflow is 40 wt% solvent on a solute-free basis, compute the flow rates and compositions of overflow and underflow.

#### 4.54. Incomplete leaching of $\text{Na}_2\text{CO}_3$ from a solid by water.

Repeat Exercise 4.53 if the residence time is sufficient to leach only 80% of the carbonate.

#### 4.55. Crystallization from a mixture of benzene and naphthalene.

A total of 6,000 lb/h of a liquid solution of 40 wt% benzene in naphthalene at 50°C is cooled to 15°C. Use Figure 4.22 to obtain

the weight of crystals and the flow rate and composition of mother liquor. Are the crystals benzene or naphthalene?

#### 4.56. Crystallization from a mixture of benzene and naphthalene.

Repeat Example 4.10, except determine the temperature necessary to crystallize 80% of the naphthalene.

#### 4.57. Cooling crystallization for a mixture of benzene and naphthalene.

Ten thousand kg/h of a 10 wt% liquid solution of naphthalene in benzene is cooled from 30°C to 0°C. Determine the amount of crystals and composition and flow rate of the mother liquor. Are the crystals benzene or naphthalene? Use Figure 4.22.

#### 4.58. Cooling crystallization of Na<sub>2</sub>SO<sub>4</sub> from an aqueous solution.

Repeat Example 4.11, except let the original solution be 20 wt% Na<sub>2</sub>SO<sub>4</sub>.

#### 4.59. Neutralization to precipitate the tetrahydrate of calcium citrate.

Although citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) can be obtained by solvent extraction from fruits (e.g., lemons and limes) and vegetables, or synthesized from acetone, most commonly it is produced by submerged, batch, aerobic fermentation of carbohydrates (e.g., dextrose, sucrose, glucose, etc.) using the pure culture of a mold such as *Aspergillus niger*. Fermentation is followed by a series of continuous downstream processing steps. First, biomass in the form of suspended or precipitated solids is removed by a rotary vacuum filter, leaving a clarified broth. For a process that produces 1,700,000 kg/yr of anhydrous citric acid crystals, the flow rate of clarified broth is 1,300 kg/h, consisting of 16.94 wt% citric acid, 82.69 wt% water, and 0.37 wt% other solutes. To separate the citric acid from the other solutes, the broth is neutralized at 50°C with the stoichiometric amount of Ca(OH)<sub>2</sub> from a 33 wt% aqueous solution, causing calcium citrate to precipitate as the tetrahydrate [Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·4H<sub>2</sub>O]. The solubility of calcium citrate in water at 50°C is 1.7 g/1,000 g H<sub>2</sub>O. (a) Write a chemical equation for the neutralization reaction to produce the precipitate. (b) Complete a component material balance in kg/h, showing in a table the broth, calcium hydroxide solution, citrate precipitate, and mother liquor.

#### 4.60. Dissolving crystals of Na<sub>2</sub>SO<sub>4</sub> with water.

At 20°C, for 1,000 kg of a mixture of 50 wt% Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O and 50 wt% Na<sub>2</sub>SO<sub>4</sub> crystals, how many kg of water must be added to completely dissolve the crystals if the temperature is kept at 20°C at equilibrium? Use Figure 4.23.

#### 4.61. Adsorption of phenol (B) from an aqueous solution.

Repeat Example 4.12, except determine the grams of activated carbon needed to achieve: (a) 75% adsorption of phenol; (b) 90% adsorption of phenol; (c) 98% adsorption of phenol.

#### 4.62. Adsorption of a colored substance from an oil by clay particles.

A colored substance (B) is removed from a mineral oil by adsorption with clay particles at 25°C. The original oil has a color index of 200 units/100 kg oil, while the decolorized oil must have an index of only 20 units/100 kg oil. The following are experimental adsorption equilibrium data measurements:

|                                 |     |     |     |     |     |
|---------------------------------|-----|-----|-----|-----|-----|
| $c_B$ , color units/100 kg oil  | 200 | 100 | 60  | 40  | 10  |
| $q_B$ , color units/100 kg clay | 10  | 7.0 | 5.4 | 4.4 | 2.2 |

(a) Fit the data to the Freundlich equation. (b) Compute the kg of clay needed to treat 500 kg of oil if one equilibrium contact is used.

### Section 4.8

#### 4.63. Absorption of acetone (A) from air by water.

Vapor–liquid equilibrium data in mole fractions for the system acetone–air–water at 1 atm (101.3 kPa) are as follows:

|                          |       |       |       |       |       |       |
|--------------------------|-------|-------|-------|-------|-------|-------|
| $y$ , acetone in air :   | 0.004 | 0.008 | 0.014 | 0.017 | 0.019 | 0.020 |
| $x$ , acetone in water : | 0.002 | 0.004 | 0.006 | 0.008 | 0.010 | 0.012 |

(a) Plot the data as (1) moles acetone per mole air versus moles acetone per mole water, (2) partial pressure of acetone versus g acetone per g water, and (3)  $y$  versus  $x$ . (b) If 20 moles of gas containing 0.015 mole-fraction acetone is contacted with 15 moles of water, what are the stream compositions? Solve graphically. Neglect water/air partitioning.

#### 4.64. Separation of air into O<sub>2</sub> and N<sub>2</sub> by absorption into water.

It is proposed that oxygen be separated from nitrogen by absorbing and desorbing air in water. Pressures from 101.3 to 10,130 kPa and temperatures between 0 and 100°C are to be used. (a) Devise a scheme for the separation if the air is 79 mol% N<sub>2</sub> and 21 mol% O<sub>2</sub>. (b) Henry's law constants for O<sub>2</sub> and N<sub>2</sub> are given in Figure 4.26. How many batch absorption steps would be necessary to make 90 mol% oxygen? What yield of oxygen (based on the oxygen feed) would be obtained?

#### 4.65. Absorption of ammonia from nitrogen into water.

A vapor mixture of equal volumes NH<sub>3</sub> and N<sub>2</sub> is contacted at 20°C and 1 atm (760 torr) with water to absorb some of the NH<sub>3</sub>. If 14 m<sup>3</sup> of this mixture is contacted with 10 m<sup>3</sup> of water, calculate the % of ammonia in the gas that is absorbed. Both  $T$  and  $P$  are maintained constant. The partial pressure of NH<sub>3</sub> over water at 20°C is:

| Partial Pressure of NH <sub>3</sub> in Air, torr | Grams of Dissolved NH <sub>3</sub> /100 g of H <sub>2</sub> O |
|--|---|
| 470  | 40  |
| 298  | 30  |
| 227  | 25  |
| 166  | 20  |
| 114  | 15  |
| 69.6   | 10  |
| 50.0   | 7.5   |
| 31.7   | 5.0   |
| 24.9   | 4.0   |
| 18.2   | 3.0   |
| 15.0   | 2.5   |
| 12.0   | 2.0   |

### Section 4.9

#### 4.66. Desublimation of phthalic anhydride from a gas.

Repeat Example 4.15 for temperatures corresponding to vapor pressures for PA of: (a) 0.7 torr, (b) 0.4 torr, (c) 0.1 torr. Plot the percentage recovery of PA vs. solid vapor pressure for 0.1 torr to 1.0 torr.

#### 4.67. Desublimation of anthraquinone (A) from nitrogen.

Nitrogen at 760 torr and 300°C containing 10 mol% anthraquinone (A) is cooled to 200°C. Calculate the % desublimation of A. Vapor pressure data for solid A are

|                       |       |       |       |       |
|-----------------------|-------|-------|-------|-------|
| $T$ , °C:             | 190.0 | 234.2 | 264.3 | 285.0 |
| Vapor pressure, torr: | 1     | 10    | 40    | 100   |



These data can be fitted to the Antoine equation (2-39) using the first three constants.

**4.68. Separation of a gas mixture of by adsorption.**

At 25°C and 101 kPa, 2 mol of a gas containing 35 mol% propylene in propane is equilibrated with 0.1 kg of silica gel adsorbent. Using Figure 4.29, calculate the moles and composition of the gas adsorbed and the gas not adsorbed.

**4.69. Separation of a gas mixture by adsorption.**

Fifty mol% propylene in propane is separated with silica gel. The products are to be 90 mol% propylene and 75 mol% propane. If 1,000 lb of silica gel/lbmol of feed gas is used, can the desired separation be made in one stage? If not, what separation can be achieved? Use Figure 4.29.

**Section 4.10**

**4.70. Crystallization of MgSO<sub>4</sub> from water by evaporation.**

Repeat Example 4.17 for 90% evaporation of the water.

**4.71. Crystallization of Na<sub>2</sub>SO<sub>4</sub> from water by evaporation.**

A 5,000-kg/h aqueous solution of 20 wt% Na<sub>2</sub>SO<sub>4</sub> is fed to an evaporative crystallizer at 60°C. Equilibrium data are given in Figure 4.23. If 80% of the Na<sub>2</sub>SO<sub>4</sub> is crystallized, calculate the: (a) kg of water that must be evaporated per hour; (b) crystallizer pressure in torr.

**4.72. Bubble, secondary dew points, and primary dew points.**

Calculate the dew-point pressure, secondary dew-point pressure, and bubble-point pressure of the following mixtures at 50°C, assuming that the aromatics and water are insoluble: (a) 50 mol% benzene

and 50 mol% water; (b) 50 mol% toluene and 50 mol% water; (c) 40 mol% benzene, 40 mol% toluene, and 20 mol% water.

**4.73. Bubble and dew points of benzene, toluene, and water mixtures.**

Repeat Exercise 4.71, except compute temperatures for a pressure of 2 atm.

**4.74. Bubble point of a mixture of toluene, ethylbenzene, and water.**

A liquid of 30 mol% toluene, 40 mol% ethylbenzene, and 30 mol% water is subjected to a continuous flash distillation at 0.5 atm. Assuming that mixtures of ethylbenzene and toluene obey Raoult's law and that the hydrocarbons are immiscible in water and vice versa, calculate the temperature and composition of the vapor phase at the bubble-point temperature.

**4.75. Bubble point, dew point, and 50 mol% flash for water-*n*-butanol.**

As shown in Figure 4.8, water (W) and *n*-butanol (B) can form a three-phase system at 101 kPa. For a mixture of overall composition of 60 mol% W and 40 mol% B, use a process simulator with the UNIFAC method to estimate: (a) dew-point temperature and composition of the first drop of liquid; (b) bubble-point temperature and composition of the first bubble of vapor; (c) compositions and relative amounts of all three phases for 50 mol% vaporization.

**4.76. Isothermal three-phase flash of six-component mixture.**

Repeat Example 4.19 for a temperature of 25°C. Are the changes significant?

## Cascades and Hybrid Systems

### §5.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Explain how multi-equilibrium-stage cascades with countercurrent flow can achieve a significantly better separation than a single equilibrium stage.
- Estimate recovery of a key component in countercurrent leaching and washing cascades, and in each of three types of liquid–liquid extraction cascades.
- Define and explain the significance of absorption and stripping factors.
- Estimate the recoveries of all components in a single-section, countercurrent cascade using the Kremser method.
- Explain why a two-section, countercurrent cascade can achieve a sharp separation between two feed components, while a single-section cascade cannot.
- Configure a membrane cascade to improve a membrane separation.
- Explain the merits and give examples of hybrid separation systems.
- Determine degrees of freedom and a set of specifications for a separation process or any element in the process.

One separation stage is rarely sufficient to produce pure commercial products. *Cascades*, which are aggregates of stages, are needed to (1) accomplish separations that cannot be achieved in a single stage, (2) reduce the amounts of mass- or energy-separating agents required, and (3) make efficient use of raw materials.

Figure 5.1 shows the type of *countercurrent cascade* prevalent in *unit operations* such as distillation, absorption, stripping, and liquid–liquid extraction. Two or more process streams of different phase states and compositions are intimately contacted to promote rapid mass and heat transfer so that the separated phases leaving the stage approach physical equilibrium. Although equilibrium conditions may not be achieved in each stage, it is common to design and analyze cascades using equilibrium-stage models. In the case of membrane separations, phase equilibrium is not a consideration and mass-transfer rates through the membrane determine the separation.

In cases where the extent of separation by a single-unit operation is limited or the energy required is excessive, *hybrid systems* of two different separation operations, such as the combination of distillation and pervaporation, can be considered. This chapter introduces both cascades and hybrid systems. To illustrate the benefits of cascades, the calculations are based on simple models. Rigorous models are deferred to Chapters 10–12.

### §5.1 CASCADE CONFIGURATIONS

Figure 5.2 shows possible cascade configurations in both horizontal and vertical layouts. Stages are represented by either boxes, as in Figure 5.1, or as horizontal lines, as in Figures 5.2d, e. In Figure 5.2, F is the feed; the mass-separating agent, if used, is S; and products are designated by  $P_i$ .

The linear *countercurrent cascade*, shown in Figures 5.1 and 5.2a, is very efficient and widely used. The linear *cross-current cascade*, shown in Figure 5.2b, is not as efficient as the countercurrent cascade, but it is convenient for batchwise configurations in that the solvent is divided into portions fed individually to each stage.

Figure 5.2c depicts a two-dimensional diamond configuration rather than a linear cascade. In batch crystallization, Feed F is separated in stage 1 into crystals, which pass to stage 2, and mother liquor, which passes to stage 4. In other stages, partial crystallization or recrystallization occurs by processing crystals, mother liquor, or combinations thereof with solvent S. Final products are purified crystals and impurity-bearing mother liquors.

Figure 5.1 and the first three cascades in Figure 5.2 consist of *single sections* of stages with streams entering and leaving only from the ends. Such cascades are used to recover components from a feed stream, but are not useful for making a sharp separation between two selected feed components, called *key components*. To do this, a cascade of *two sections* of stages is used, e.g., the countercurrent cascade of Figure 5.2d, which consists of one section above the feed and

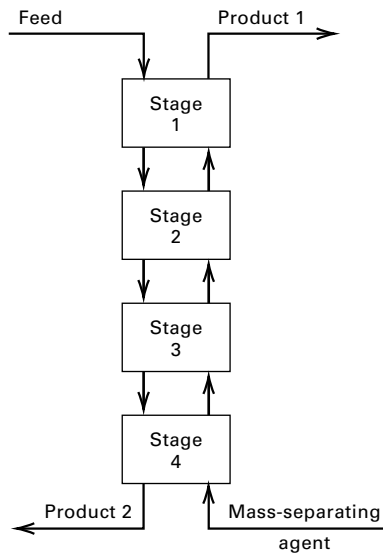


Figure 5.1 Cascade of contacting stages.

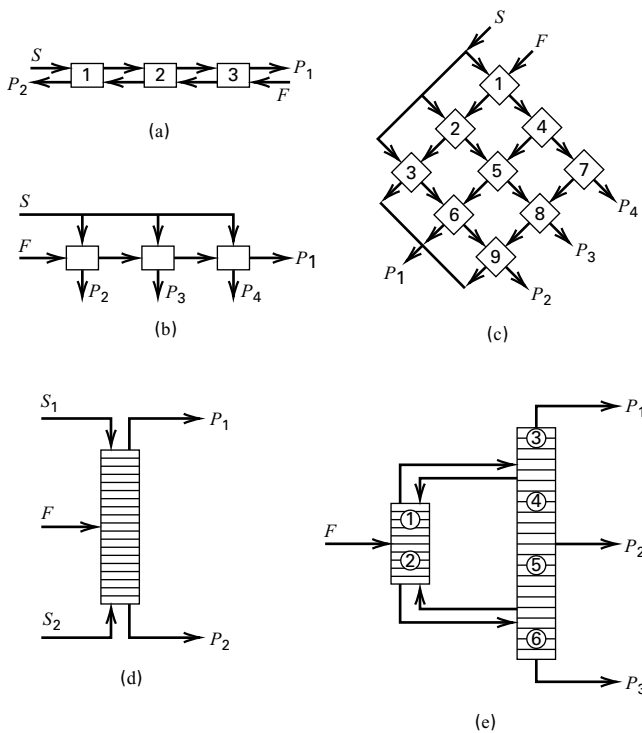


Figure 5.2 Cascade configurations: (a) countercurrent; (b) crosscurrent; (c) two-dimensional, diamond; (d) two-section, countercurrent; (e) interlinked system of countercurrent cascades.

one below. If  $S_2$  is boiling vapor produced by steam or partial vaporization of  $P_2$  by a boiler, and  $S_1$  is liquid reflux produced by partial condensation of  $P_1$ , this is a simple distillation column. If two solvents are used, where  $S_1$  selectively dissolves certain components of the feed while  $S_2$  is more selective for the other components, the process is *fractional liquid-liquid extraction*.

Figure 5.2e is an interlinked system of two distillation columns containing six countercurrent cascade sections. Reflux and boilup for the first column are provided by the second column. This system can take a three-component feed,  $F$ , and produce three almost pure products,  $P_1$ ,  $P_2$ , and  $P_3$ .

In this chapter, a countercurrent, single-section cascade for a leaching or washing process is considered first. Then, cocurrent, crosscurrent, and countercurrent single-section cascades are compared for a liquid-liquid extraction process. After that, a single-section, countercurrent cascade is developed for a vapor-liquid absorption operation. Finally, membrane cascades are described. In the first three cases, a set of linear algebraic equations is reduced to a single relation for estimating the extent of separation as a function of the number of stages, the separation factor, and the ratio of mass- or energy-separating agent to the feed. In later chapters it will be seen that for cascade systems, easily solved equations cannot be obtained from rigorous models, making calculations with a process simulator a necessity.

### §5.2 SOLID-LIQUID CASCADES

The  $N$ -stage, countercurrent leaching-washing process in Figure 5.3 is an extension of the single-stage systems in §4.7. The solid feed entering stage 1 consists of two components, A and B, of mass flow rates  $F_A$  and  $F_B$ . Pure solvent, C, which enters stage  $N$  at flow rate  $S$ , dissolves solute B but not insoluble carrier A. The concentrations of B are expressed in terms of mass ratios of solute-to-solvent,  $Y$ . Thus, the liquid overflow from each stage,  $j$ , contains  $Y_j$  mass of soluble material per mass of solute-free solvent. The underflow is a slurry consisting of a mass flow  $F_A$  of insoluble solids; a constant ratio of mass of solvent-to-mass of insoluble solids,  $R$ ; and  $X_j$  mass of soluble material-to-mass of solute-free solvent. For a given feed, a relationship between the exiting underflow concentration of the soluble component,  $X_N$ ; the solvent feed rate,  $S$ ; and the number of stages,  $N$ , is derived next.

All soluble material, B, in the feed is leached in stage 1, and all other stages are then washing stages for reducing the amount of soluble material lost in the underflow leaving the last stage,  $N$ , thereby increasing the amount of soluble material leaving in the overflow from stage 1. By solvent material balances, for constant  $R$  the flow rate of solvent leaving in the

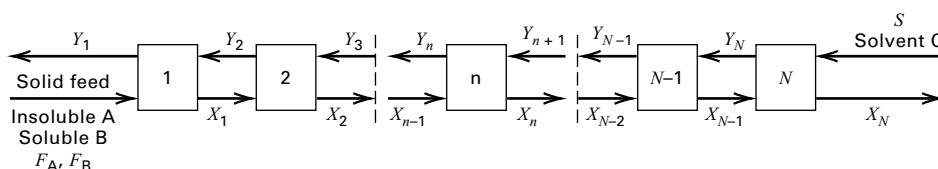


Figure 5.3 Countercurrent leaching or washing system.

overflow from stages 2 to  $N$  is  $S$ . The flow rate of solvent leaving in the underflow from stages 1 to  $N$  is  $RF_A$ . Therefore, the flow rate of solvent leaving in the overflow from stage 1 is  $S - RF_A$ .

A material balance for soluble material B around any interior stage  $n$  from  $n = 2$  to  $N - 1$  is

$$Y_{n+1}S + X_{n-1}RF_A = Y_nS + X_nRF_A \quad (5-1)$$

For terminal stages 1 and  $N$ , the material balances on the soluble material are, respectively,

$$Y_2S + F_B = Y_1(S - RF_A) + X_1RF_A \quad (5-2)$$

$$X_{N-1}RF_A = Y_NS + X_NRF_A \quad (5-3)$$

Assuming equilibrium, the concentration of B in each overflow equals the concentration of B in the liquid part of the underflow from the same stage. Thus,

$$X_n = Y_n \quad (5-4)$$

In addition, it is convenient to define a *washing factor*,  $W$ , as

$$W = \frac{S}{RF_A} \quad (5-5)$$

If (5-1), (5-2), and (5-3) are each combined with (5-4) to eliminate  $Y$ , and the resulting equations are rearranged to allow substitution of (5-5), then,

$$X_1 - X_2 = \left(\frac{F_B}{S}\right) \quad (5-6)$$

$$\left(\frac{1}{W}\right)X_{n-1} - \left(\frac{1+W}{W}\right)X_n + X_{n+1} = 0, \quad (5-7)$$

$n = 2 \text{ to } N - 1$

$$\left(\frac{1}{W}\right)X_{N-1} - \left(\frac{1+W}{W}\right)X_N = 0 \quad (5-8)$$

Equations (5-6) to (5-8) are a set of  $N$  linear equations in  $N$  unknowns,  $X_n$  ( $n = 1$  to  $N$ ). The equations form a tridiagonal, sparse matrix. For example, with  $N = 5$ ,

$$\begin{bmatrix} 1 & -1 & 0 & 0 & 0 \\ \left(\frac{1}{W}\right) & -\left(\frac{1+W}{W}\right) & 1 & 0 & 0 \\ 0 & \left(\frac{1}{W}\right) & -\left(\frac{1+W}{W}\right) & 1 & 0 \\ 0 & 0 & \left(\frac{1}{W}\right) & -\left(\frac{1+W}{W}\right) & 1 \\ 0 & 0 & 0 & \left(\frac{1}{W}\right) & -\left(\frac{1+W}{W}\right) \end{bmatrix} \times \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix} = \begin{bmatrix} \left(\frac{F_B}{S}\right) \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (5-9)$$

Equations of type (5-9) are solved by Gaussian elimination by eliminating unknowns  $X_1, X_2$ , etc., to obtain

$$X_N = \left(\frac{F_B}{S}\right) \left(\frac{1}{W^{N-1}}\right) \quad (5-10)$$

By back-substitution, interstage values of  $X$  are given by

$$X_n = \left(\frac{F_B}{S}\right) \left(\frac{\sum_{k=0}^{N-n} W^k}{W^{N-1}}\right) \quad (5-11)$$

For example, with  $N = 5$ ,

$$X_1 = Y_1 = \left(\frac{F_B}{S}\right) \left(\frac{1 + W + W^2 + W^3 + W^4}{W^4}\right)$$

The cascade, for any given  $S$ , maximizes  $Y_1$ , the amount of B dissolved in the solvent leaving stage 1, and minimizes  $X_N$ , the amount of B dissolved in the solvent leaving with A from stage  $N$ . Equation (5-10) indicates that this can be achieved for feed rate  $F_B$  by specifying a large solvent feed,  $S$ , a large number of stages,  $N$ , and/or by employing a large washing factor,  $W$ , which can be achieved by minimizing the amount of liquid underflow compared to overflow. It should be noted that the minimum amount of solvent required corresponds to zero overflow from stage 1,

$$S_{\min} = RF_A \quad (5-12)$$

For this minimum value,  $W = 1$  from (5-5), and all soluble solids leave in the underflow from the last stage,  $N$ , regardless of the number of stages; hence it is best to specify a value of  $S$  significantly greater than  $S_{\min}$ . Equations (5-10) and (5-5) show that the value of  $X_N$  is reduced exponentially by increasing  $N$ . Thus, the countercurrent cascade is very effective. For two or more stages,  $X_N$  is also reduced exponentially by increasing  $S$ . For three or more stages, the value of  $X_N$  is reduced exponentially by decreasing  $R$ .

### EXAMPLE 5.1 Leaching of $\text{Na}_2\text{CO}_3$ with Water.

Water is used to dissolve 1,350 kg/h of  $\text{Na}_2\text{CO}_3$  from 3,750 kg/h of a solid, where the balance is an insoluble oxide. If 4,000 kg/h of water is used as the solvent and the total underflow from each stage is 40 wt% solvent on a solute-free basis, compute and plot the % recovery of carbonate in the overflow product for one stage and for two to five countercurrent stages, as in Figure 5.3.

#### Solution

Soluble solids feed rate =  $F_B = 1,350$  kg/h

Insoluble solids feed rate =  $F_A = 3,750 - 1,350 = 2,400$  kg/h

Solvent feed rate =  $S = 4,000$  kg/h

Underflow ratio =  $R = 40/60 = 2/3$

Washing factor =  $W = S/RF_A = 4,000/[(2/3)(2,400)] = 2.50$

Overall fractional recovery of soluble solids =  $Y_1(S - RF_A)/F_B$

By overall material balance on soluble solids for  $N$  stages,

$$F_B = Y_1(S - RF_A) + X_NRF_A$$

Solving for  $Y_1$  and using (5-5),

$$Y_1 = \frac{(F_B/S) - (1/W)X_N}{(1 - 1/W)}$$

From the given data,

$$Y_1 = \frac{(1.350/4.000) - (1/2.50)X_N}{(1 - 1/2.50)} \quad \text{or} \quad (1)$$

$$Y_1 = 0.5625 - 0.6667X_N$$

where, from (5-10),

$$X_N = \left( \frac{1.350}{4.000} \right) \frac{1}{2.50^{N-1}} = \frac{0.3375}{2.50^{N-1}} \quad (2)$$

The percent recovery of soluble material is

$$Y_1(S - RF_A)/F_B = Y_1[4,000 - (2/3)(2,400)]/1,350 \times 100\% = 177.8Y_1 \quad (3)$$

Results for one to five stages, as computed from (1) to (3), are

| No. of Stages in Cascade, $N$ | $X_N$   | $Y_1$  | Percent Recovery of Soluble Solids |
|-------------------------------|---------|--------|------------------------------------|
| 1                             | 0.3375  | 0.3375 | 60.0                               |
| 2                             | 0.1350  | 0.4725 | 84.0                               |
| 3                             | 0.0540  | 0.5265 | 93.6                               |
| 4                             | 0.0216  | 0.5481 | 97.4                               |
| 5                             | 0.00864 | 0.5567 | 99.0                               |

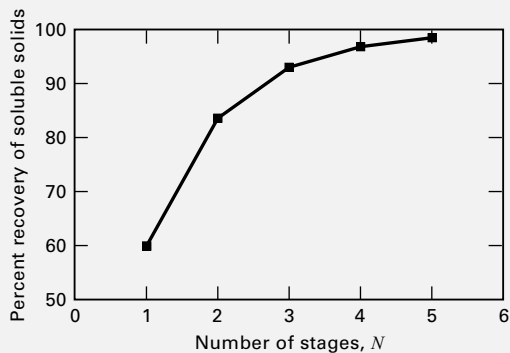


Figure 5.4 Effect of number of stages on percent recovery in Example 5.1.

A plot of the % recovery of B is shown in Figure 5.4. Only a 60% recovery is obtained with one stage, but 99% recovery is achieved for five stages. For 99% recovery with one stage, a water rate of 160,000 kg/h is required, which is 40 times that required for five stages! Thus, use of a countercurrent cascade is more effective than an excess of mass-separating agent in a single stage.

### §5.3 SINGLE-SECTION, EXTRACTION CASCADES

Two-stage cocurrent, crosscurrent, and countercurrent, single-section, liquid-liquid extraction cascades are shown in Figure 5.5. The countercurrent arrangement is generally preferred because, as will be shown, this arrangement results in a higher degree of extraction for a given amount of solvent and number of equilibrium stages.

Equation (4-25) (for the fraction of solute, B, that is not extracted) was derived for a single liquid-liquid equilibrium extraction stage, assuming the use of pure solvent and a constant value for the distribution coefficient,  $K'_{DB}$ , of B dissolved in components A and C, which are mutually insoluble. That equation is in terms of  $X_B$ , the ratio of mass of solute B to the mass of A, the other component in the feed, and the extraction factor

$$E = K'_{DB}S/F_A \quad (5-13)$$

where

$$K'_{DB} = Y_B/X_B \quad (5-14)$$

and  $Y_B$  is the ratio of mass of solute B to the mass of solvent C in the solvent-rich phase.

#### §5.3.1 Cocurrent Cascade

In Figure 5.5a, the fraction of B not extracted in stage 1 is from (4-25),

$$X_B^{(1)}/X_B^{(F)} = \frac{1}{1 + E} \quad (5-15)$$

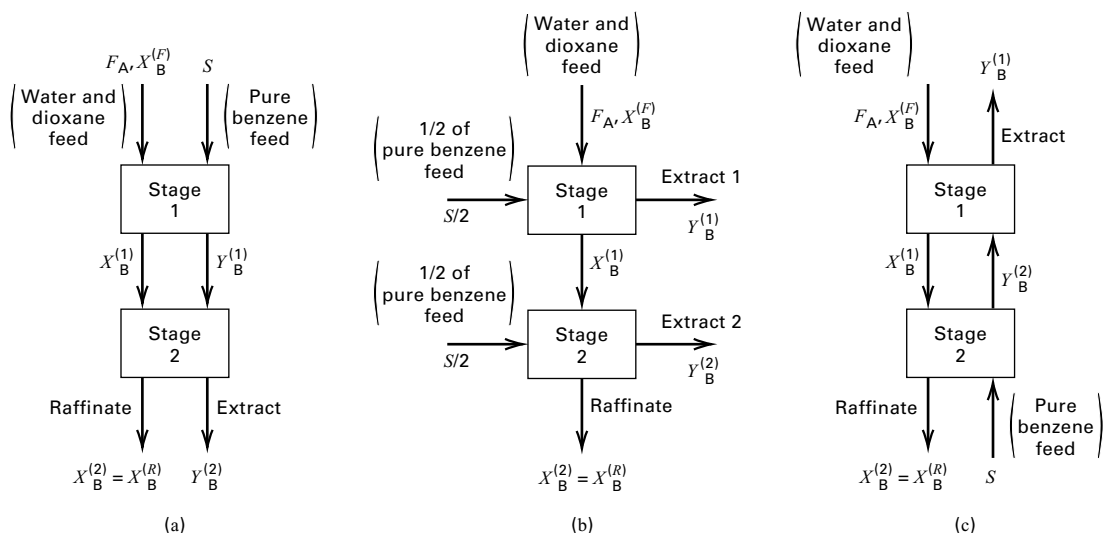


Figure 5.5 Two-stage arrangements: (a) cocurrent cascade; (b) crosscurrent cascade; (c) countercurrent cascade.

Since  $Y_B^{(1)}$  is in equilibrium with  $X_B^{(1)}$ , combining (5-15) with (5-14) to eliminate  $X_B^{(1)}$  gives

$$Y_B^{(1)}/X_B^{(F)} = K'_{D_B}/(1 + E) \quad (5-16)$$

For the second stage, a material balance for B gives

$$X_B^{(1)}F_A + Y_B^{(1)}S = X_B^{(2)}F_A + Y_B^{(2)}S \quad (5-17)$$

with 
$$K'_{D_B} = Y_B^{(2)}/X_B^{(2)} \quad (5-18)$$

However, no additional extraction can take place after the first stage because the two streams leaving are already at equilibrium when they are recontacted in subsequent stages. Accordingly, a cocurrent cascade has no merit unless required residence times are so long that equilibrium is not achieved in one stage and further capacity is needed. Regardless of the number of cocurrent equilibrium stages,  $N$ ,

$$\frac{X_B^{(N)}}{X_B^{(F)}} = \frac{1}{1 + E} \quad (5-19)$$

### §5.3.2 Crosscurrent Cascade

For the crosscurrent cascade in Figure 5.5b, the feed progresses through each stage, starting with stage 1. The solvent flow rate,  $S$ , is divided into portions that are sent to each stage. If the portions are equal, the following mass ratios are obtained by application of (4-25), where  $S$  is replaced by  $S/N$  so that  $E$  is replaced by  $E/N$ :

$$\begin{aligned} X_B^{(1)}/X_B^{(F)} &= 1/(1 + E/N) \\ X_B^{(2)}/X_B^{(1)} &= 1/(1 + E/N) \\ &\vdots \\ X_B^{(N)}/X_B^{(N-1)} &= 1/(1 + E/N) \end{aligned} \quad (5-20)$$

Combining equations in (5-20) to eliminate intermediate-stage variables,  $X_B^{(n)}$ , the final raffinate mass ratio is

$$X_B^{(N)}/X_B^{(F)} = X_B^{(R)}/X_B^{(F)} = \frac{1}{(1 + E/N)^N} \quad (5-21)$$

Interstage values of  $X_B^{(n)}$  are obtained similarly from

$$X_B^{(n)}/X_B^{(F)} = \frac{1}{(1 + E/N)^n} \quad (5-22)$$

The value of  $X_B$  decreases in each successive stage. For an infinite number of equilibrium stages, (5-21) becomes

$$X_B^{(\infty)}/X_B^{(F)} = 1/\exp(E) \quad (5-23)$$

Thus, even for an infinite number of stages,  $X_B^{(R)} = X_B^{(\infty)}$  cannot be reduced to zero to give a perfect extraction.

### §5.3.3 Countercurrent Cascade

In the countercurrent arrangement in Figure 5.5c, the feed liquid passes through the cascade countercurrently to the solvent. For a two-stage system, the material-balance and equilibrium equations for solute B for each stage are:

$$\text{Stage 1: } X_B^{(F)}F_A + Y_B^{(2)}S = X_B^{(1)}F_A + Y_B^{(1)}S \quad (5-24)$$

$$K'_{D_B} = \frac{Y_B^{(1)}}{X_B^{(1)}} \quad (5-25)$$

$$\text{Stage 2: } X_B^{(1)}F_A = X_B^{(2)}F_A + Y_B^{(2)}S \quad (5-26)$$

$$K'_{D_B} = \frac{Y_B^{(2)}}{X_B^{(2)}} \quad (5-27)$$

Combining (5-24) to (5-27) with (5-14) to eliminate  $Y_B^{(1)}$ ,  $Y_B^{(2)}$ , and  $X_B^{(1)}$  gives

$$X_B^{(2)}/X_B^{(F)} = X_B^{(R)}/X_B^{(F)} = \frac{1}{1 + E + E^2} \quad (5-28)$$

Extending (5-28) to  $N$  countercurrent stages,

$$\boxed{X_B^{(R)}/X_B^{(F)} = 1 / \left[ \sum_{n=0}^{N-1} E^n \right] = \frac{E - 1}{E^{N+1} - 1}} \quad (5-29)$$

Interstage values of  $X_B^{(n)}$  are given by

$$X_B^{(n)}/X_B^{(F)} = \sum_{k=0}^{N-n} E^k / \sum_{k=0}^N E^k \quad (5-30)$$

The decrease of  $X_B$  for countercurrent flow is greater than that for crosscurrent flow, and the difference increases exponentially with increasing extraction factor,  $E$ . Thus, the countercurrent cascade is the most efficient.

Can a perfect extraction be achieved with a countercurrent cascade? For an infinite number of equilibrium stages, the limit of (5-28) gives two results, depending on the value of the extraction factor,  $E$ :

$$X_B^{(\infty)}/X_B^{(F)} = 0, \quad 1 \leq E \leq \infty \quad (5-31)$$

$$X_B^{(\infty)}/X_B^{(F)} = (1 - E), \quad E \leq 1 \quad (5-32)$$

Thus, complete extraction can be achieved in a countercurrent cascade with an infinite  $N$  if extraction factor  $E > 1$ .

#### EXAMPLE 5.2 Extraction with Different Cascade Arrangements.

Ethylene glycol is catalytically dehydrated to *p*-dioxane (a cyclic diether) by the reaction  $2\text{HOCH}_2\text{CH}_2\text{HO} \rightarrow \text{H}_2\text{CCH}_2\text{OCH}_2\text{CH}_2\text{O} + 2\text{H}_2\text{O}$ . Water and *p*-dioxane have normal boiling points of 100°C and 101.1°C, respectively, and cannot be separated economically by distillation. However, liquid–liquid extraction at 25°C using benzene as a solvent is possible. A feed of 4,536 kg/h of a 25 wt% solution of *p*-dioxane in water is to be separated continuously with 6,804 kg/h of benzene. Assuming benzene and water are mutually insoluble, determine the effect of the number and arrangement of stages on the percent extraction of *p*-dioxane. The flowsheet is in Figure 5.6.

#### Solution

Three arrangements of stages are examined: (a) cocurrent, (b) crosscurrent, and (c) countercurrent. Because water and benzene are assumed mutually insoluble, (5-15), (5-21), and (5-29) can be used to estimate  $X_B^{(R)}/X_B^{(F)}$ , the fraction of dioxane not extracted, as a

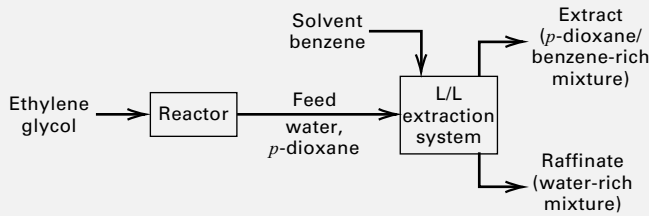


Figure 5.6 Flowsheet for Example 5.2.

function of stages. From the equilibrium data of Berdt and Lynch [1], the distribution coefficient for *p*-dioxane,  $K'_{D_B} = Y_B/X_B$ , where  $Y$  is the benzene phase and  $X$  the water phase, varies from 1.0 to 1.4; assume a value of 1.2. From the given data,  $S = 6,804$  kg/h of benzene,  $F_A = 4,536(0.75) = 3,402$  kg/h of water, and  $X_B^{(F)} = 0.25/0.75 = 1/3$ . From (5-13),  $E = 1.2(6,804)/3,402 = 2.4$ .

**Single equilibrium stage:**

All arrangements give identical results for one stage. By (5-15),

$$X_B^{(1)}/X_B^{(F)} = 1/(1 + 2.4) = 0.294$$

The corresponding fractional extraction is

$$1 - X_B^{(1)}/X_B^{(F)} = 1 - 0.294 = 0.706 \text{ or } 70.6\%$$

**More than one equilibrium stage:**

(a) Cocurrent: For any number of stages, extraction is still only 70.6%.

(b) Crosscurrent: For any number of stages, (5-21) applies. For two stages, assuming equal flow of solvent to each stage,

$$X_B^{(2)}/X_B^{(F)} = 1/(1 + E/2)^2 = 1/(1 + 2.4/2)^2 = 0.207$$

and extraction is 79.3%. Results for other  $N$  are in Figure 5.7.

(c) Countercurrent: (5-29) applies. For example, for two stages,

$$X_B^{(2)}/X_B^{(F)} = 1/(1 + E + E^2) = 1/(1 + 2.4 + 2.4^2) = 0.109$$

and extraction is 89.1%. Results for other  $N$  are in Figure 5.7, where a probability-scale ordinate is convenient because for the countercurrent case with  $E > 1$ , 100% extraction is approached as  $N \rightarrow \infty$ .

For the crosscurrent arrangement, the maximum extraction from (5-23) is 90.9%, while for five stages, the countercurrent cascade achieves 99% extraction.

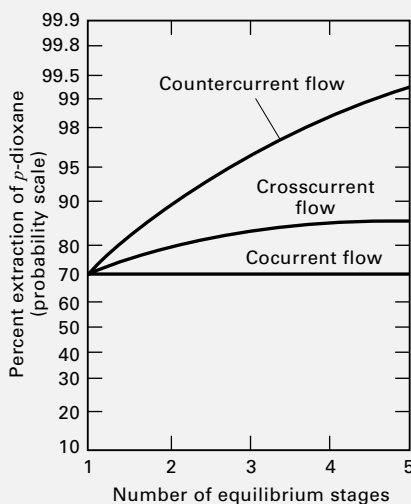


Figure 5.7 Effect of multiple stages on extraction efficiency.

**§5.4 MULTICOMPONENT VAPOR–LIQUID CASCADES**

Countercurrent cascades are used extensively for vapor–liquid separation operations, including absorption, stripping, and distillation. For absorption and stripping, a *single-section cascade* is used to recover one selected component from the feed. The approximate calculation procedure in this section relates compositions of multicomponent vapor and liquid streams entering and exiting the cascade to the number of equilibrium stages. This procedure is called a *group method* because it provides only an overall treatment of a group of stages in the cascade, without considering detailed changes in temperature, phase compositions, and flows from stage to stage.

**§5.4.1 Single-Section Cascades by Group Methods**

Kremser [2] originated the group method by deriving an equation for absorption or stripping in a multistage, countercurrent absorber. The treatment here is similar to that of Edmister [3]. An alternative treatment is given by Smith and Brinkley [4].

Consider first a countercurrent absorber of  $N$  adiabatic, equilibrium stages in Figure 5.8a, where stages are numbered from top to bottom. The absorbent is pure, and component molar flow rates are  $v_i$  and  $l_i$ , in the vapor and liquid phases, respectively. In the following derivation, the subscript  $i$  is dropped. A material balance around the top, including stages 1 through  $N - 1$ , for any absorbed species is

$$v_N = v_1 + l_{N-1} \tag{5-33}$$

where

$$v = yV \tag{5-34}$$

$$l = xL \tag{5-35}$$

and  $l_0 = 0$ . The equilibrium  $K$ -value at stage  $N$  is

$$y_N = K_N x_N \tag{5-36}$$

Combining (5-34), (5-35), and (5-36),  $v_N$  becomes

$$v_N = \frac{l_N}{L_N/(K_N V_N)} \tag{5-37}$$

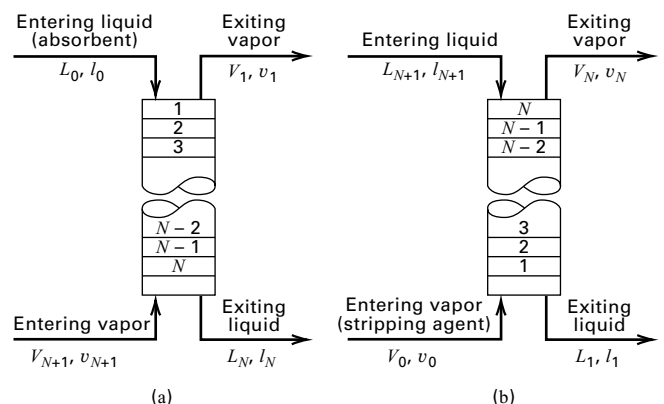


Figure 5.8 Countercurrent cascades of  $N$  adiabatic stages: (a) absorber; (b) stripper.

An absorption factor  $A$ , analogous to the extraction factor,  $E$ , for a given stage and component is defined by

$$A = \frac{L}{KV} \quad (5-38)$$

Combining (5-37) and (5-38),

$$v_N = \frac{l_N}{A_N} \quad (5-39)$$

Substituting (5-39) into (5-33),

$$l_N = (l_{N-1} + v_1)A_N \quad (5-40)$$

The flow rate,  $l_{N-1}$ , is eliminated by successive substitution using material balances around successively smaller sections of the top of the cascade. For stages 1 through  $N - 2$ ,

$$l_{N-1} = (l_{N-2} + v_1)A_{N-1} \quad (5-41)$$

Substituting (5-41) into (5-40),

$$l_N = l_{N-2}A_{N-1}A_N + v_1(A_N + A_{N-1}A_N) \quad (5-42)$$

Continuing to the top stage, where  $l_1 = v_1A_1$ , converts (5-42) to

$$l_N = v_1(A_1A_2A_3 \dots A_N + A_2A_3 \dots A_N + A_3 \dots A_N + \dots + A_N) \quad (5-43)$$

Combining (5-43) with the overall component balance,

$$l_N = v_{N+1} - v_1 \quad (5-44)$$

gives an equation for the exiting vapor in terms of the entering vapor and a recovery fraction,  $\phi_A$ :

$$v_1 = v_{N+1}\phi_A \quad (5-45)$$

where, by definition, the recovery fraction is

$$\phi_A = \frac{1}{A_1A_2A_3 \dots A_N + A_2A_3 \dots A_N + A_3 \dots A_N + \dots + A_N + 1} \\ = \text{fraction of species in entering vapor that is not absorbed} \quad (5-46)$$

In the group method, an average, effective absorption factor,  $A_e$ , replaces the separate absorption factors for each stage, simplifying (5-46) to

$$\phi_A = \frac{1}{A_e^N + A_e^{N-1} + A_e^{N-2} + \dots + A_e + 1} \quad (5-47)$$

When multiplied and divided by  $(A_e - 1)$ , (5-47) reduces to the Kremser equation:

$$\phi_A = \frac{A_e - 1}{A_e^{N+1} - 1} \quad (5-48)$$

Because each component has a different  $A_e$ , it has a different  $\phi_A$ . Figure 5.9 from Edmister [3] is a plot of (5-48) with a probability scale for  $\phi_A$ , a logarithmic scale for  $A_e$ , and  $N$  as a parameter. This plot, in linear coordinates, was first developed by Kremser [2].

Consider next the stripper shown in Figure 5.8b. Assume the components stripped from the liquid are absent in the entering vapor, and ignore absorption of the stripping agent. Stages are numbered from bottom to top. The pertinent

stripping equations follow in a manner analogous to the absorber equations. The results are

$$l_1 = l_{N+1}\phi_S \quad (5-49)$$

where

$$\phi_S = \frac{S_e - 1}{S_e^{N+1} - 1} \\ = \text{fraction of species in entering} \\ \text{liquid that is not stripped} \quad (5-50)$$

$$S = \frac{KV}{L} = \frac{1}{A} = \text{stripping factor} \quad (5-51)$$

Figure 5.9 also applies to (5-50). As shown in Figure 5.10, absorbers are frequently coupled with strippers or distillation columns to permit regeneration and recycle of absorbent. Since stripping action is not perfect, recycled absorbent contains species present in the vapor feed. Up-flowing vapor strips these as well as absorbed species in the makeup absorbent. A general absorber equation is obtained by combining (5-45) for absorption with a form of (5-49) for stripping species from the entering liquid. For stages numbered from top to bottom, as in Figure 5.8a, (5-49) becomes:

$$l_N = l_0\phi_S \quad (5-52)$$

or, since

$$l_0 = v_1 + l_N \\ v_1 = l_0(1 - \phi_S) \quad (5-53)$$

A balance for a component in both entering vapor and entering liquid is obtained by adding (5-45) and (5-53):

$$v_1 = v_{N+1}\phi_A + l_0(1 - \phi_S) \quad (5-54)$$

which applies to each component in the entering vapor. Equation (5-52) is for species appearing only in the entering liquid. The analogous equation for a stripper is

$$l_1 = l_{N+1}\phi_S + v_0(1 - \phi_A) \quad (5-55)$$

### EXAMPLE 5.3 Absorption of Hydrocarbons by Oil.

In Figure 5.11, the heavier components in a superheated hydrocarbon gas are to be removed by absorption at 400 psia with a high-molecular-weight oil. Estimate exit vapor and liquid flow rates and compositions by the Kremser method, using estimated component absorption and stripping factors from the entering values of  $L$  and  $V$ , and the component  $K$ -values below based on an average entering temperature of  $(90 + 105)/2 = 97.5^\circ\text{F}$ .

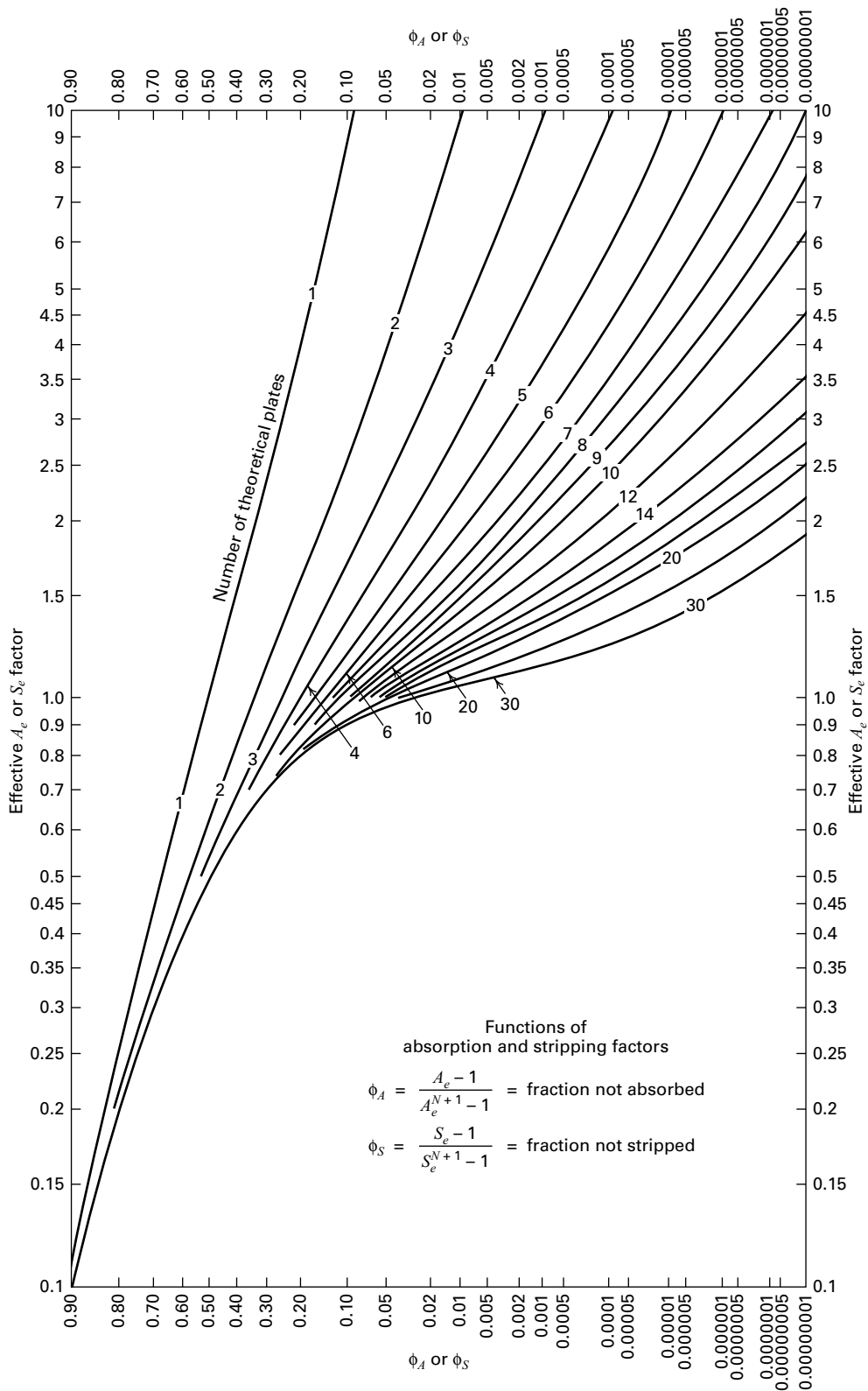
#### Solution

From (5-38) and (5-51),  $A_i = L/K_iV = 165/[K_i(800)] = 0.206/K_i$ ;  $S_i = 1/A_i = 4.85K_i$ ; and  $N = 6$  stages. Values of  $\phi_A$  and  $\phi_S$  are from (5-48) and (5-50) or Figure 5.9. Values of  $(v_i)_1$  are from (5-54). Values of  $(l_i)_6$ , in the exit liquid, are computed from an overall component material balance using Figure 5.8a:

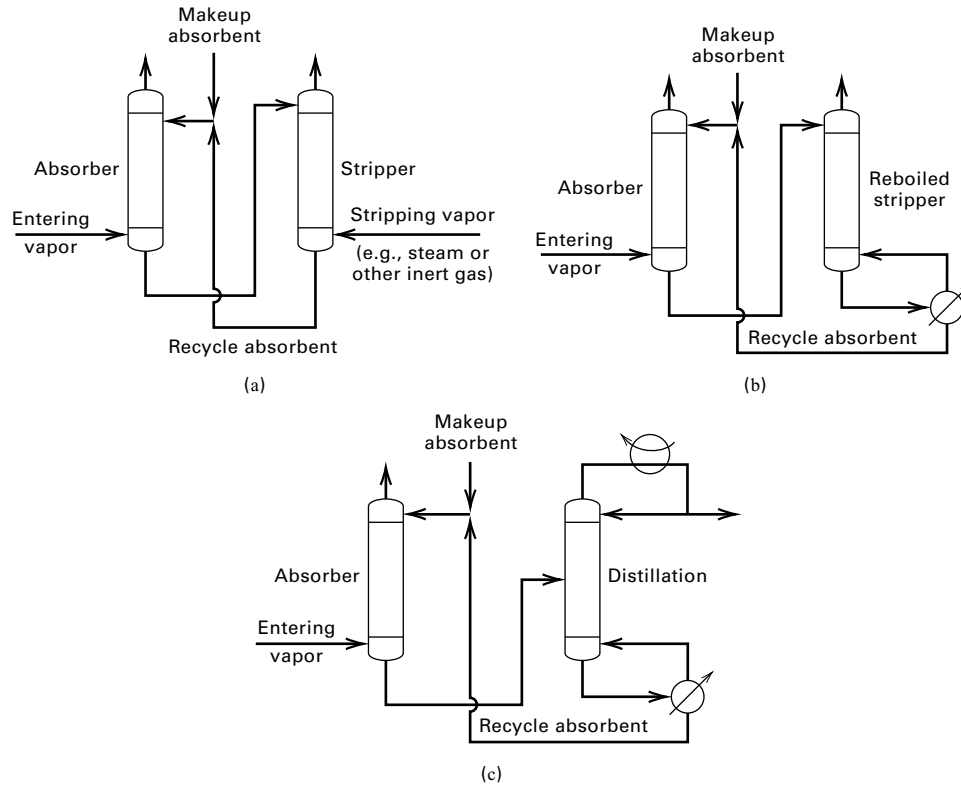
$$(l_i)_6 = (l_i)_0 + (v_i)_7 - (v_i)_1 \quad (1)$$

The computations, made with a spreadsheet, give the following results:





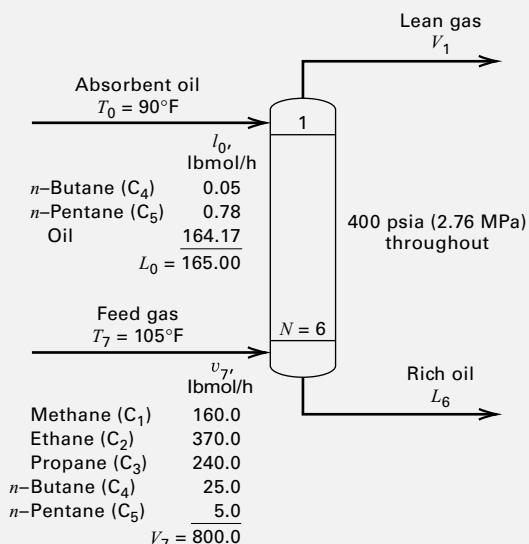
**Figure 5.9** Plot of Kremser equation for a single-section, countercurrent cascade.  
 [From W.C. Edmister, *AIChE J.*, 3, 165–171 (1957).]



**Figure 5.10** Various coupling schemes for absorbent recovery: (a) use of steam or inert gas stripper; (b) use of reboiled stripper; (c) use of distillation.

| Component | $K@97.5^\circ\text{F}, 400\text{ psia}$ | $A$    | $S$    | $\phi_A$ | $\phi_S$ | $v_1$   | $l_6$   |
|-----------|---|--------|--------|----------|----------|---------|---------|
| $C_1$     | 6.65                                    | 0.0310 | —      | 0.969    | —        | 155.0   | 5.0     |
| $C_2$     | 1.64                                    | 0.126  | —      | 0.874    | —        | 323.5   | 46.5    |
| $C_3$     | 0.584                                   | 0.353  | —      | 0.647    | —        | 155.4   | 84.6    |
| $nC_4$    | 0.195                                   | 1.06   | 0.946  | 0.119    | 0.168    | 3.02    | 22.03   |
| $nC_5$    | 0.0713                                  | 2.89   | 0.346  | 0.00112  | 0.654    | 0.28    | 5.5     |
| Oil       | 0.0001                                  | —      | 0.0005 | —        | 0.9995   | 0.075   | 164.095 |
|           |   |        |        |          |          | 637.275 | 327.725 |

The results indicate that approximately 20% of the gas is absorbed. Less than 0.1% of the absorbent oil is stripped.

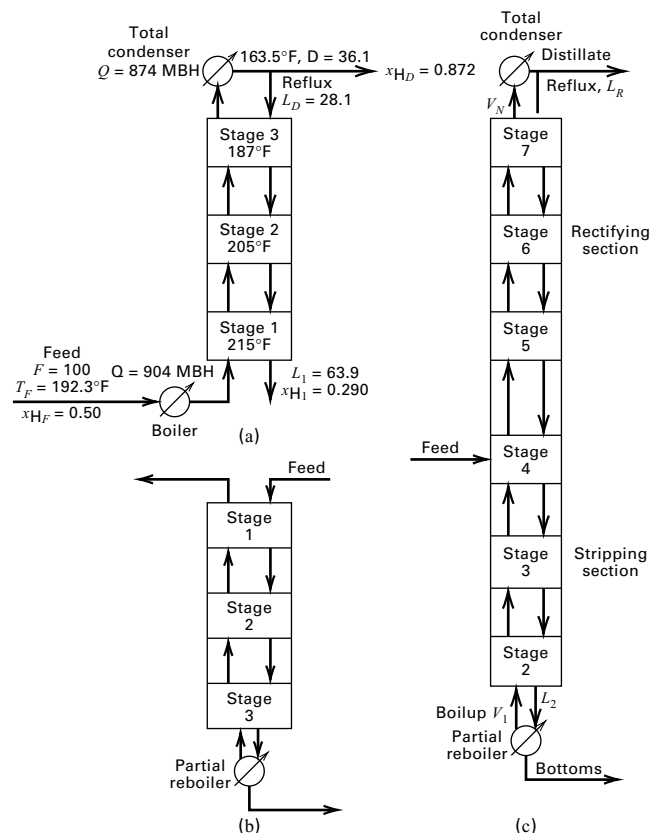


**Figure 5.11** Specifications for absorber of Example 5.3.

### §5.4.2 Two-Section Cascades

A single-section, countercurrent cascade of the type shown in Figure 5.8 cannot make a sharp separation between two *key components* of a feed. Instead, a two-section, countercurrent cascade, as shown in Figure 5.2d, is required. Consider the distillation of 100 lbmol/h of an equimolar mixture of  $n$ -hexane and  $n$ -octane at the bubble point at 1 atm. Let this mixture be heated by a boiler to the dew point. In Figure 5.12a, this vapor mixture is sent to a single-section cascade of three equilibrium stages. Instead of using liquid absorbent as in Figure 5.8a, the vapor leaving the top stage is condensed, with the liquid being divided into a distillate product and a reflux that is returned to the top stage. The reflux selectively absorbs  $n$ -octane so that the distillate is enriched in the more-volatile  $n$ -hexane. This set of stages is called a *rectifying section*.

To enrich the liquid leaving stage 1 in  $n$ -octane, that liquid becomes the feed to a second single-section cascade of three stages, as shown in Figure 5.12b. The purpose of this



**Figure 5.12** Development of a two-section cascade: (a) rectifying section; (b) stripping section; (c) multistage distillation.

cascade, called a *stripping section*, is similar to that of the stripper shown in Figure 5.8b. However, instead of using a stripping vapor, the liquid leaving the bottom stage enters a partial reboiler that produces the stripping vapor and a bottoms product rich in *n*-octane.

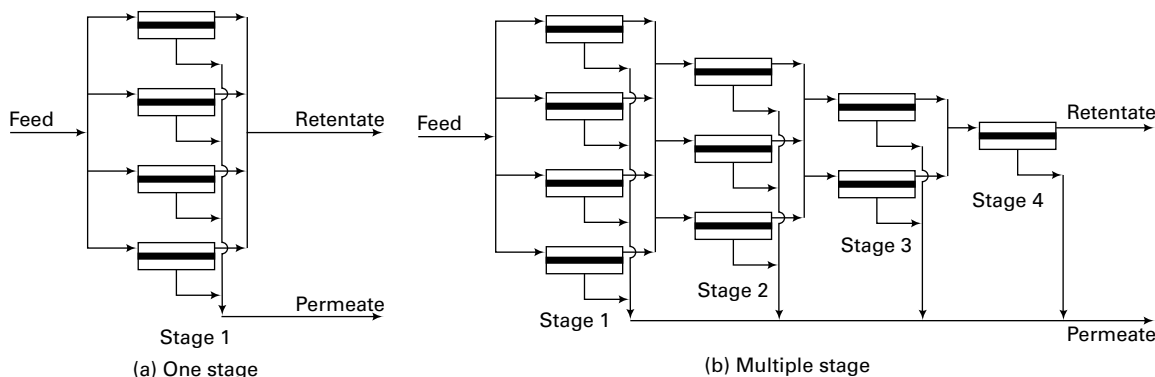
Vapor leaving the top of the bottom section is combined with the vapor feed to the top section, resulting in a distillation column shown in Figure 5.12c. Two-section cascades of this type are the industrial workhorses of the chemical industry because they produce nearly pure liquid and vapor products. The two-section cascade in Figure 5.12c is applied to the distillation of binary mixtures in Chapter 7 and multi-component mixtures in Chapters 9 and 10.

### §5.5 MEMBRANE CASCADES

Membrane-separation systems often consist of multiple-membrane modules because a single module may not be large enough to handle the required feed rate. Figure 5.13a shows a number of modules of identical size in parallel with retentates and permeates from each module combined. For example, a membrane-separation system for separating hydrogen from methane might require a membrane area of 9,800 ft<sup>2</sup>. If the largest membrane module available has 3,300 ft<sup>2</sup> of membrane surface, three modules in parallel are required. The parallel units function as a single stage. If, in addition, a large fraction of the feed is to become permeate, it may be necessary to carry out the membrane separation in two or more stages, as shown in Figure 5.13b for four stages, with the number of modules reduced for each successive stage as the flow rate on the feed-retentate side of the membrane decreases. The combined retentate from each stage becomes the feed for the next stage. The combined permeates for each stage, which differ in composition from stage to stage, are combined to give the final permeate, as shown in Figure 5.13b, where required interstage compressors and/or pumps are not shown.

Single-membrane stages are often limited in the degree of separation and recovery achievable. In some cases, a high purity can be obtained, but only at the expense of a low recovery. In other cases, neither a high purity nor a high recovery can be obtained. The following table gives two examples of the separation obtained for a single stage of gas permeation using a commercial membrane.

| Feed Molar Composition                    | More Permeable Component | Product Molar Composition                                   | Percent Recovery                      |
|---|--------------------------|---|---------------------------------------|
| 85% H <sub>2</sub><br>15% CH <sub>4</sub> | H <sub>2</sub>           | 99% H <sub>2</sub> ,<br>1% CH <sub>4</sub> in the permeate  | 60% of H <sub>2</sub><br>in the feed  |
| 80% CH <sub>4</sub><br>20% N <sub>2</sub> | N <sub>2</sub>           | 97% CH <sub>4</sub> ,<br>3% N <sub>2</sub> in the retentate | 57% of CH <sub>4</sub><br>in the feed |



**Figure 5.13** Parallel units of membrane separators.

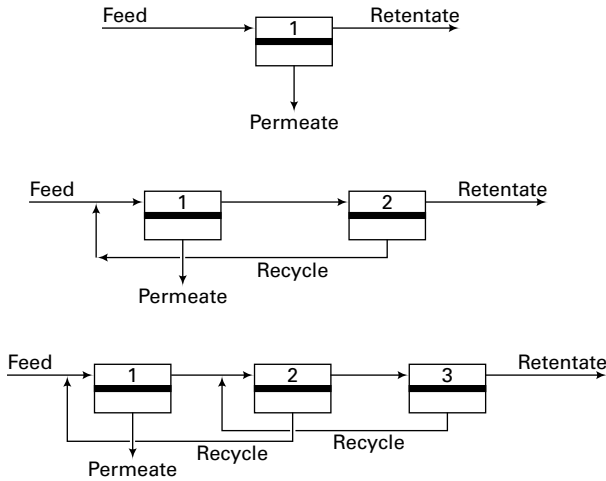


Figure 5.14 Membrane cascades.

In the first example, the permeate purity is quite high, but the recovery is not. In the second example, the purity of the retentate is reasonably high, but the recovery is not. To improve purity and recovery, membrane stages are cascaded with recycle. Shown in Figure 5.14 are three membrane-separation systems, studied by Prasad et al. [5] for the production of pure nitrogen (retentate) from air, using a membrane material that is more permeable to oxygen. The first system is just a single stage. The second system is a cascade of two stages, with recycle of permeate from the second to the first stage. The third system is a cascade of three stages with permeate recycles from stage 3 to stage 2 and stage 2 to stage 1. The two cascades are similar to the single-section, countercurrent stripping cascade shown in Figure 5.8b. Prasad et al. [5] give the following results for the three configurations in Figure 5.14:

| Membrane System | Mol% N <sub>2</sub> in Retentate | % Recovery of N <sub>2</sub> |
|-----------------|----------------------------------|------------------------------|
| Single Stage    | 98                               | 45                           |
| Two Stage       | 99.5                             | 48                           |
| Three Stage     | 99.9                             | 50                           |

Thus, high purities are obtained with a single-section membrane cascade, but little improvement in the recovery is provided by additional stages. To obtain both high purity and high recovery, a two-section membrane cascade is necessary, as discussed in §14.3.

§5.6 HYBRID SYSTEMS

Hybrid systems, encompassing two or more different separation operations in series, have the potential for reducing energy and raw-material costs and accomplishing difficult separations. Table 5.1 lists hybrid systems used commercially that have received considerable attention. Examples of applications are included. Not listed in Table 5.1 are hybrid systems consisting of distillation combined with extractive

Table 5.1 Hybrid Systems

| Hybrid System                                | Separation Example                                       |
|--|--|
| Adsorption—gas permeation                    | Nitrogen—Methane   |
| Simulated moving bed adsorption—distillation | Metaxylene-paraxylene with ethylbenzene eluent           |
| Chromatography—crystallization               | —  |
| Crystallization—distillation                 | —  |
| Crystallization—pervaporation                | —  |
| Crystallization—liquid–liquid extraction     | Sodium carbonate—water                                   |
| Distillation—adsorption                      | Ethanol—water  |
| Distillation—crystallization                 | —  |
| Distillation—gas permeation                  | Propylene—propane  |
| Distillation—pervaporation                   | Ethanol—water  |
| Gas permeation—absorption                    | Dehydration of natural gas                               |
| Reverse osmosis—distillation                 | Carboxylic acids—water                                   |
| Reverse osmosis—evaporation                  | Concentration of wastewater                              |
| Stripper—gas permeation                      | Recovery of ammonia and hydrogen sulfide from sour water |

distillation, azeotropic distillation, and/or liquid–liquid extraction, which are considered in Chapter 11.

The first example in Table 5.1 is a hybrid system that combines pressure-swing adsorption (PSA), to preferentially remove methane, with a gas-permeation membrane operation to remove nitrogen. The permeate is recycled to the adsorption step. Figure 5.15 compares this hybrid system to a single-stage gas-permeation membrane and a single-stage pressure-swing adsorption. Only the hybrid system is capable of making a sharp separation between methane and nitrogen. Products obtainable from these three processes are compared in Table 5.2 for 100,000 scfh of feed containing 80% methane and 20% nitrogen. For all processes, the methane-rich

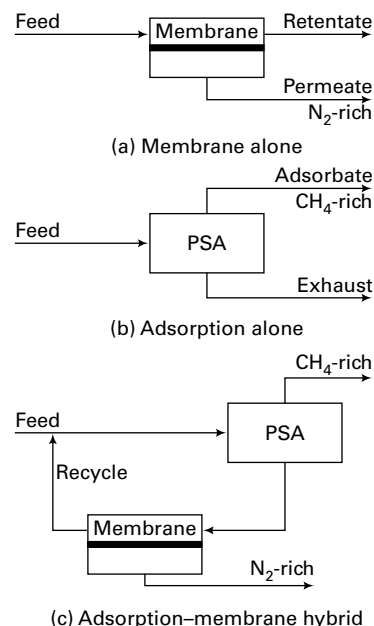


Figure 5.15 Separation of methane from nitrogen.

**Table 5.2** Typical Products for Processes in Figure 5.15

|                       | Flow Rate,<br>Mscfh | Mol%<br>CH <sub>4</sub> | Mol%<br>N <sub>2</sub> |
|-----------------------|---------------------|-------------------------|------------------------|
| Feed gas              | 100                 | 80                      | 20                     |
| Membrane only:        |                     |                         |                        |
| Retentate             | 47.1                | 97                      | 3                      |
| Permeate              | 52.9                | 65                      | 35                     |
| PSA only:             |                     |                         |                        |
| Adsorbate             | 70.6                | 97                      | 3                      |
| Exhaust               | 29.4                | 39                      | 61                     |
| Hybrid system:        |                     |                         |                        |
| CH <sub>4</sub> -rich | 81.0                | 97                      | 3                      |
| N <sub>2</sub> -rich  | 19.0                | 8                       | 92                     |

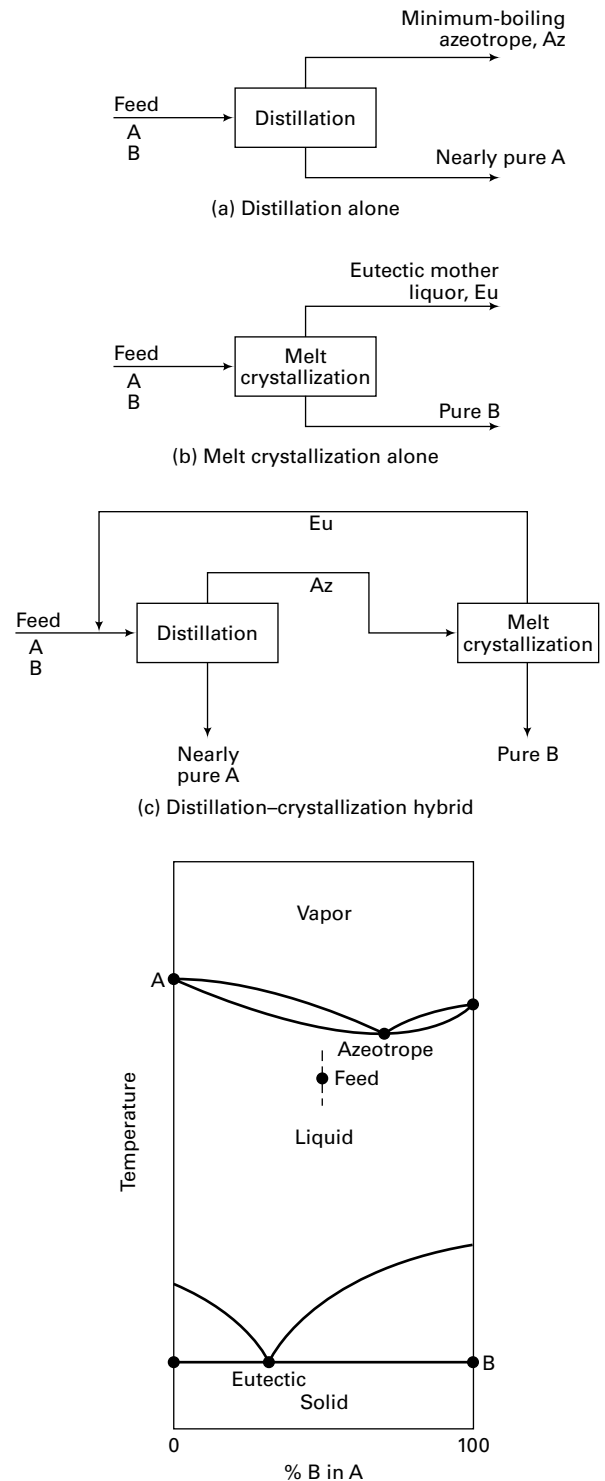
product contains 97 mol% methane. Only the hybrid system gives a nitrogen-rich product of greater than 90 mol%, and a high recovery of methane (98%). The methane recovery for a membrane alone is only 57%, while the adsorber gives 86%.

No application is shown in Table 5.1 for crystallization and distillation. However, there is much interest in these processes because Berry and Ng [6] show that such systems can overcome limitations of eutectics in crystallization and azeotropes in distillation. Furthermore, although solids are more difficult to process than fluids, crystallization requires just a single stage to obtain high purity. Figure 5.16 includes one of the distillation and crystallization hybrid configurations of Berry and Ng [6]. The feed of A and B, as shown in the phase diagram, forms an azeotrope in the vapor–liquid region, and a eutectic in the liquid–solid region at a lower temperature. The feed composition in Figure 5.16d lies between the eutectic and azeotropic compositions. If distillation alone is used, the distillate composition approaches that of the minimum-boiling azeotrope, Az, and the bottoms approaches pure A. If melt crystallization is used, the products are crystals of pure B and a mother liquor approaching the eutectic, Eu. The hybrid system in Figure 5.16 combines distillation with melt crystallization to produce pure B and nearly pure A. The feed is distilled and the distillate of near-azeotropic composition is sent to the melt crystallizer. Here, the mother liquor of near-eutectic composition is recovered and recycled to the distillation column. The net result is near-pure A obtained as bottoms from distillation and pure B obtained from the crystallizer.

The combination of distillation and membrane pervaporation for separating azeotropic mixtures, particularly ethanol–water, is also receiving considerable attention. Distillation produces a bottoms of nearly pure water and an azeotrope distillate that is sent to the pervaporation step, which produces a nearly pure ethanol retentate and a water-rich permeate that is recycled to the distillation step.

## §5.7 DEGREES OF FREEDOM AND SPECIFICATIONS FOR CASCADES

The solution to a multicomponent, multiphase, multistage separation problem involves material-balance, energy-balance, and phase-equilibria equations. This implies that a sufficient



(d) Phase diagram for distillation–crystallization hybrid system.

**Figure 5.16** Separation of an azeotropic- and eutectic-forming mixture.

number of design variables should be specified so that the number of remaining unknown variables equals the number of independent equations relating the variables. The degrees-of-freedom analysis discussed in §4.1 for a single equilibrium stage is now extended to one- and multiple-section cascades. Although the extension is for continuous, steady-state processes, similar extensions can be made for batch and semi-continuous processes.

An intuitively simple, but operationally complex, method of finding  $N_D$ , the number of independent design variables (*degrees of freedom*, or *variance*), as developed by Kwauk [7], is to enumerate all variables,  $N_V$ , and to subtract the total number of independent equations,  $N_E$ , that relate the variables:

$$N_D = N_V - N_E \quad (5-56)$$

Typically, there are intensive variables such as pressure, composition, and temperature; extensive variables such as flow and heat-transfer rates; and equipment parameters such as number of stages. Physical properties such as enthalpy or  $K$ -values are not counted because they are functions of intensive variables. The variables are relatively easy to enumerate, but to achieve an unambiguous count of  $N_E$ , it is necessary to find all independent relationships due to mass and energy conservations, phase-equilibria restrictions, process specifications, and equipment configurations.

Separation equipment consists of physically identifiable elements: equilibrium stages, condensers, reboilers, pumps, etc., as well as stream dividers and stream mixers. It is helpful to examine each element separately before considering the complete system.

### §5.7.1 Stream Variables

A complete specification of intensive variables for a single-phase stream consists of  $C$  mole fractions plus  $T$  and  $P$ , or  $C + 2$  variables. However, only  $C - 1$  of the mole fractions are independent, because the other mole fraction must satisfy the mole-fraction constraint:

$$\sum_{i=1}^c \text{mole fractions} = 1.0$$

Thus,  $C + 1$  intensive stream variables can be specified. This is in agreement with the Gibbs phase rule (4-1), which states that, for a single-phase system, the intensive variables are specified by  $C - \mathcal{P} + 2 = C + 1$  variables. To this number can be added the total flow rate, an extensive variable. Although the missing mole fraction is often treated implicitly, it is preferable to include all mole fractions in the list of stream variables and then to include, in the equations, the above mole-fraction constraint, from which the missing mole fraction is calculated. Thus, for each stream there are  $C + 3$  variables. For example, for a liquid stream, the variables are liquid mole fractions  $x_1, x_2, \dots, x_C$ ; total flow rate  $L$ ; temperature  $T$ ; and pressure  $P$ .

### §5.7.2 Adiabatic or Nonadiabatic Equilibrium Stage

For an equilibrium-stage element with two entering and two exiting streams, as in Figure 5.17, the variables are those associated with the four streams plus the heat-transfer rate. Thus,

$$N_V = 4(C + 3) + 1 = 4C + 13$$

The exiting streams  $V_{OUT}$  and  $L_{OUT}$  are in equilibrium, so there are equilibrium equations as well as component material balances, a total material balance, an energy balance, and mole-fraction constraints. The equations relating these variables and  $N_E$  are

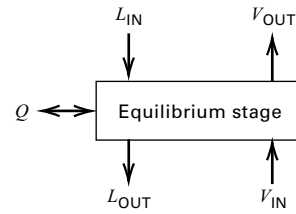


Figure 5.17 Equilibrium stage with heat addition.

| Equations   | Number of Equations |
|---|---------------------|
| Pressure equality<br>$P_{V_{OUT}} = P_{L_{OUT}}$  | 1                   |
| Temperature equality,<br>$T_{V_{OUT}} = T_{L_{OUT}}$  | 1                   |
| Phase-equilibrium relationships,<br>$(y_i)_{V_{OUT}} = K_i(x_i)_{L_{OUT}}$  | $C$                 |
| Component material balances,<br>$L_{IN}(x_i)_{L_{IN}} + V_{IN}(y_i)_{V_{IN}} = L_{OUT}(x_i)_{L_{OUT}} + V_{OUT}(y_i)_{V_{OUT}}$ | $C - 1$             |
| Total material balance,<br>$L_{IN} + V_{IN} = L_{OUT} + V_{OUT}$  | 1                   |
| Energy balance,<br>$Q + h_{L_{IN}}L_{IN} = h_{V_{IN}}V_{IN} = h_{L_{OUT}}L_{OUT} + h_{V_{OUT}}V_{OUT}$                          | 1                   |
| Mole-fraction constraints in entering and exiting streams<br>e.g., $\sum_{i=1}^C (x_i)_{L_{IN}} = 1$                            | 4                   |
|   | $N_E = 2C + 7$      |

Alternatively,  $C$ , instead of  $C - 1$ , component material balances can be written. The total material balance is then a dependent equation obtained by summing the component material balances and applying the mole-fraction constraints to eliminate mole fractions. From (5-56),

$$N_D = (4C + 13) - (2C + 7) = 2C + 6$$

Several different sets of design variables can be specified. The following typical set includes complete specification of the two entering streams as well as stage pressure and heat-transfer rate.

| Variable Specification                                  | Number of Variables |
|---|---------------------|
| Component mole fractions, $(x_i)_{L_{IN}}$              | $C - 1$             |
| Total flow rate, $L_{IN}$                               | 1                   |
| Component mole fractions, $(y_i)_{V_{IN}}$              | $C - 1$             |
| Total flow rate, $V_{IN}$                               | 1                   |
| Temperature and pressure of $L_{IN}$                    | 2                   |
| Temperature and pressure of $V_{IN}$                    | 2                   |
| Stage pressure, $(P_{V_{OUT}} \text{ or } P_{L_{OUT}})$ | 1                   |
| Heat transfer rate, $Q$                                 | 1                   |
|   | $N_D = 2C + 6$      |

Specification of these  $(2C + 6)$  variables permits calculation of the unknown variables  $L_{OUT}$ ,  $V_{OUT}$ ,  $(x_C)_{L_{IN}}$ ,  $(y_C)_{V_{IN}}$ , all  $(x_i)_{L_{OUT}}$ ,  $T_{OUT}$ , and all  $(y_i)_{V_{OUT}}$ , where  $C$  denotes the missing mole fractions in the two entering streams.

### §5.7.3 Single-Section, Countercurrent Cascade

The single-section, countercurrent cascade unit in Figure 5.18 contains  $N$  of the adiabatic or nonadiabatic stage elements shown in Figure 5.17. For enumerating variables, equations, and degrees of freedom for combinations of such elements, the number of design variables for the unit is obtained by summing the variables associated with each element and then subtracting from the total variables, the  $C + 3$  variables for each of the  $N_R$  redundant, interconnecting streams that arise when the output of one element becomes the input to another. Also, if an unspecified number of repetitions, e.g., stages, occurs within the unit, an additional variable is added, one for each group of repetitions, giving a total of  $N_A$  additional variables. The number of independent equations for the unit is obtained by summing the values of  $N_E$  for the units and then subtracting the  $N_R$  redundant mole-fraction constraints. The number of degrees of freedom is obtained as before, from (5-56). Thus,

$$(N_V)_{\text{unit}} = \sum_{\text{all elements, } e} (N_V)_e - N_R(C + 3) + N_A \quad (5-57)$$

$$(N_E)_{\text{unit}} = \sum_{\text{all elements, } e} (N_E)_e - N_R \quad (5-58)$$

Combining (5-56), (5-57), and (5-58),

$$(N_D)_{\text{unit}} = \sum_{\text{all elements, } e} (N_D)_e - N_R(C + 2) + N_A \quad (5-59)$$

or 
$$(N_D)_{\text{unit}} = (N_V)_{\text{unit}} - (N_E)_{\text{unit}} \quad (5-60)$$

For the  $N$ -stage cascade unit of Figure 5.18, with reference to the above degrees-of-freedom analysis for the single adiabatic or nonadiabatic equilibrium-stage element, the total

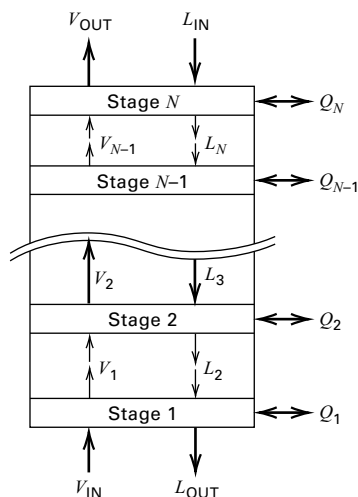


Figure 5.18 An  $N$ -stage single-section cascade.

number of variables from (5-57) is

$$\begin{aligned} (N_V)_{\text{unit}} &= N(4C + 13) - [2(N - 1)](C + 3) + 1 \\ &= 7N + 2NC + 2C + 7 \end{aligned}$$

since  $2(N - 1)$  interconnecting streams exist. The additional variable is the total number of stages (i.e.,  $N_A = 1$ ). The number of independent relationships from (5-58) is

$$(N_E)_{\text{unit}} = N(2C + 7) - 2(N - 1) = 5N + 2NC + 2$$

since  $2(N - 1)$  redundant mole-fraction constraints exist. The number of degrees of freedom from (5-60) is

$$(N_D)_{\text{unit}} = N_V - N_E = 2N + 2C + 5$$

Note, again, that the coefficient of  $C$  is 2, the number of streams entering the cascade. For a cascade, the coefficient of  $N$  is always 2 (corresponding to  $P$  and  $Q$  for each stage). One possible set of design variables is:

| Variable Specification                              | Number of Variables |
|---|---------------------|
| Heat-transfer rate for each stage (or adiabaticity) | $N$                 |
| Stage pressures                                     | $N$                 |
| Stream $V_{IN}$ variables                           | $C + 2$             |
| Stream $L_{IN}$ variables                           | $C + 2$             |
| Number of stages                                    | 1                   |
|   | $2N + 2C + 5$       |

Output variables for this specification include missing mole fractions for  $V_{IN}$  and  $L_{IN}$ , stage temperatures, and variables associated with  $V_{OUT}$ ,  $L_{OUT}$ , and interstage streams.  $N$ -stage cascade units represent absorbers, strippers, and extractors.

### §5.7.4 Two-Section, Countercurrent Cascades

Two-section, countercurrent cascades can consist not only of adiabatic or nonadiabatic equilibrium-stage elements, but also elements shown in Table 5.3 for total and partial reboilers; total and partial condensers; stages with a feed,  $F$ , or sidestream  $S$ ; and stream mixers and dividers. These elements can be combined into any of a number of complex cascades by applying to Eqs. (5-57) through (5-60) the values of  $N_V$ ,  $N_E$ , and  $N_D$  given in Table 5.3 for the other elements.

The design or simulation of multistage separation operations involves solving relationships for output variables after selecting values of design variables to satisfy the degrees of freedom. Two common cases exist: (1) the *design case*, in which recovery specifications are made and the number of required equilibrium stages is determined; and (2) the *simulation case*, in which the number of stages is specified and product separations are computed. The second case is less complex computationally because the number of stages is specified, thus predetermining the number of equations to be solved. Table 5.4 is a summary of possible variable specifications for each of the two cases for a number of separator types discussed in Chapter 1 and shown in Table 1.1. For all separators in Table 5.4, it is assumed that all inlet streams are completely specified, and that all element and unit pressures and heat-transfer rates (except for condensers and reboilers)

**Table 5.3** Degrees of Freedom for Separation Operation Elements and Units

|     | Schematic | Element or Unit Name                                 | $N_V$ , Total Number of Variables | $N_E$ , Independent Relationships | $N_D$ , Degrees of Freedom |
|-----|-----------|--|-----------------------------------|-----------------------------------|----------------------------|
| (a) |           | Total boiler (reboiler)                              | $(2C + 7)$                        | $(C + 3)$                         | $(C + 4)$                  |
| (b) |           | Total condenser                                      | $(2C + 7)$                        | $(C + 3)$                         | $(C + 4)$                  |
| (c) |           | Partial (equilibrium) boiler (reboiler)              | $(3C + 10)$                       | $(2C + 6)$                        | $(C + 4)$                  |
| (d) |           | Partial (equilibrium) condenser                      | $(3C + 10)$                       | $(2C + 6)$                        | $(C + 4)$                  |
| (e) |           | Adiabatic equilibrium stage                          | $(4C + 12)$                       | $(2C + 7)$                        | $(2C + 5)$                 |
| (f) |           | Equilibrium stage with heat transfer                 | $(4C + 13)$                       | $(2C + 7)$                        | $(2C + 6)$                 |
| (g) |           | Equilibrium feed stage with heat transfer and feed   | $(5C + 16)$                       | $(2C + 8)$                        | $(3C + 8)$                 |
| (h) |           | Equilibrium stage with heat transfer and sidestream  | $(5C + 16)$                       | $(3C + 9)$                        | $(2C + 7)$                 |
| (i) |           | $N$ -connected equilibrium stages with heat transfer | $(7N + 2NC + 2C + 7)$             | $(5N + 2NC + 2)$                  | $(2N + 2C + 5)$            |
| (j) |           | Stream mixer   | $(3C + 10)$                       | $(C + 4)$                         | $(2C + 6)$                 |
| (k) |           | Stream divider                                       | $(3C + 10)$                       | $(2C + 5)$                        | $(C + 5)$                  |

<sup>a</sup>Sidestream can be vapor or liquid.

<sup>b</sup>Alternatively, all streams can be vapor.

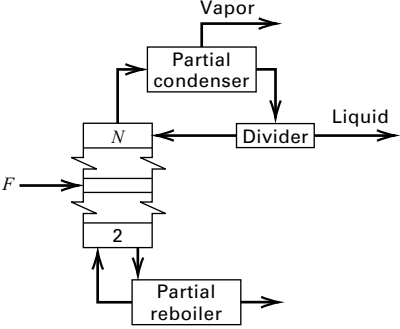
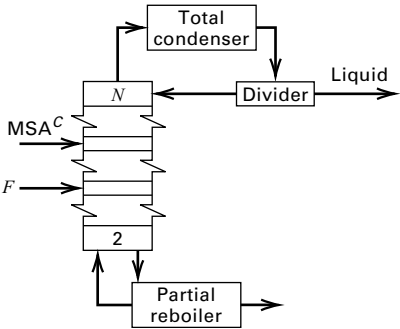
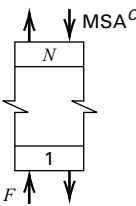
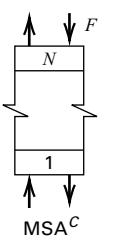


**Table 5.4** Typical Variable Specifications for Design Cases

| Unit Operation  | $N_D$          | Variable Specification <sup>a</sup>  |   |
|---|----------------|--|---|
|   |                | Case I, Component Recoveries Specified   | Case II, Number of Equilibrium Stages Specified   |
| (a) Absorption (two inlet streams)  | $2N + 2C + 5$  | 1. Recovery of one key component   | 1. Number of stages   |
| (b) Distillation (one inlet stream, total condenser, partial reboiler)                          | $2N + C + 9$   | 1. Condensate at saturation temperature<br>2. Recovery of light-key component<br>3. Recovery of heavy-key component<br>4. Reflux ratio (> minimum)<br>5. Optimal feed stage <sup>b</sup> | 1. Condensate at saturation temperature<br>2. Number of stages above feed stage<br>3. Number of stages below feed stage<br>4. Reflux ratio<br>5. Distillate flow rate |
| (c) Distillation (one inlet stream, partial condenser, partial reboiler, vapor distillate only) | $(2N + C + 6)$ | 1. Recovery of light key component<br>2. Recovery of heavy key component<br>3. Reflux ratio (> minimum)<br>4. Optimal feed stage <sup>b</sup>  | 1. Number of stages above feed stage<br>2. Number of stages below feed stage<br>3. Reflux ratio<br>4. Distillate flow rate  |
| (d) Liquid-liquid extraction with two solvents (three inlet streams)                            | $2N + 3C + 8$  | 1. Recovery of key component 1<br>2. Recovery of key component 2   | 1. Number of stages above feed<br>2. Number of stages below feed  |
| (e) Reboiled absorption (two inlet streams)   | $2N + 2C + 6$  | 1. Recovery of light-key component<br>2. Recovery of heavy-key component<br>3. Optimal feed stage <sup>b</sup>   | 1. Number of stages above feed<br>2. Number of stages below feed<br>3. Bottoms flow rate  |
| (f) Reboiled stripping (one inlet stream)   | $2N + C + 3$   | 1. Recovery of one key component<br>2. Reboiler heat duty <sup>d</sup>   | 1. Number of stages<br>2. Bottoms flow rate   |

(Continued)

Table 5.4 (Continued)

| Unit Operation  | $N_D$          | Variable Specification <sup>a</sup>  |   |
|---|----------------|--|---|
|   |                | Case I, Component Recoveries Specified   | Case II, Number of Equilibrium Stages Specified   |
| <p>(g) Distillation (one inlet stream, partial condenser, partial reboiler, both liquid and vapor distillates)</p>   | $2N + C + 9$   | <ol style="list-style-type: none"> <li>1. Ratio of vapor distillate to liquid distillate</li> <li>2. Recovery of light-key component</li> <li>3. Recovery of heavy-key component</li> <li>4. Reflux ratio (&gt; minimum)</li> <li>5. Optimal feed stage<sup>b</sup></li> </ol>                                 | <ol style="list-style-type: none"> <li>1. Ratio of vapor distillate to liquid distillate</li> <li>2. Number of stages above feed stage</li> <li>3. Number of stages below feed stage</li> <li>4. Reflux ratio</li> <li>5. Liquid distillate flow rate</li> </ol>  |
| <p>(h) Extractive distillation (two inlet streams, total condenser, partial reboiler, single-phase condensate)</p>  | $2N + 2C + 12$ | <ol style="list-style-type: none"> <li>1. Condensate at saturation temperature</li> <li>2. Recovery of light-key component</li> <li>3. Recovery of heavy-key component</li> <li>4. Reflux ratio (&gt; minimum)</li> <li>5. Optimal feed stage<sup>b</sup></li> <li>6. Optimal MSA stage<sup>b</sup></li> </ol> | <ol style="list-style-type: none"> <li>1. Condensate at saturation temperature</li> <li>2. Number of stages above MSA stage</li> <li>3. Number of stages between MSA and feed stages</li> <li>4. Number of stages below feed stage</li> <li>5. Reflux ratio</li> <li>6. Distillate flow rate</li> </ol> |
| <p>(i) Liquid-liquid extraction (two inlet streams)</p>    | $2N + 2C + 5$  | <ol style="list-style-type: none"> <li>1. Recovery of one key component</li> </ol>   | <ol style="list-style-type: none"> <li>1. Number of stages</li> </ol>   |
| <p>(j) Stripping (two inlet streams)</p>   | $2N + 2C + 5$  | <ol style="list-style-type: none"> <li>1. Recovery of one key component</li> </ol>   | <ol style="list-style-type: none"> <li>1. Number of stages</li> </ol>   |

<sup>a</sup>Does not include the following variables, which are also assumed specified: all inlet stream variables ( $C + 2$  for each stream); all element and unit pressures; all element and unit heat-transfer rates except for condensers and reboilers.

<sup>b</sup>Optimal stage for introduction of inlet stream corresponds to minimization of total stages.

<sup>c</sup>For case I variable specifications, MSA flow rates must be greater than minimum values for specified recoveries.

<sup>d</sup>For case I variable specifications, reboiler heat duty must be greater than minimum value for specified recovery.

are specified. Thus, only variable specifications satisfying the remaining degrees of freedom are listed.

**EXAMPLE 5.4 Specifications for a Distillation Column.**

Consider the multistage distillation column in Figure 5.19, which has one feed, one sidestream, a total condenser, a partial reboiler, and heat transfer to or from stages. Determine the number of degrees of freedom and a reasonable set of specifications.

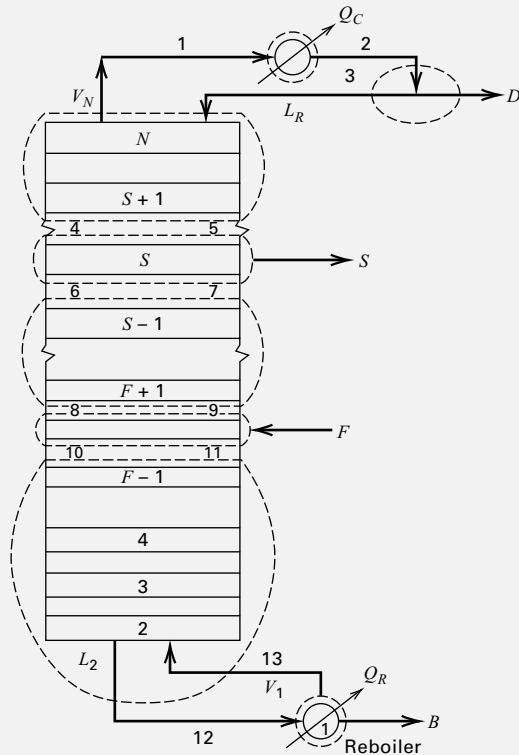


Figure 5.19 Complex distillation unit.

**Solution**

The separator is assembled from the circled elements and units of Table 5.3. The total variables are determined by summing the variables  $(N_V)_e$  for each element from Table 5.3 and subtracting redundant variables due to interconnecting flows. Redundant mole-fraction constraints are subtracted from the sum of independent relationships for each element  $(N_E)_e$ . This problem was first treated by Gilliland and Reed [8] and more recently by Kwauk [7]. Differences in  $N_D$  obtained by various authors are due, in part, to how stages are numbered. Here, the partial reboiler is the first equilibrium stage. From Table 5.3, element variables and relationships are as follows:

| Element or Unit      | $(N_V)_e$                                 | $(N_E)_e$                            |
|----------------------|---|--------------------------------------|
| Total condenser      | $(2C + 7)$                                | $(C + 3)$                            |
| Reflux divider       | $(3C + 10)$                               | $(2C + 5)$                           |
| $(N - S)$ stages     | $[7(N - S) + 2(N - S)C + 2C + 7]$         | $[5(N - S) + 2(N - S)C + 2]$         |
| Sidestream stage     | $(5C + 16)$                               | $(3C + 9)$                           |
| $(S - 1) - F$ stages | $[7(S - 1 - F) + 2(S - 1 - F)C + 2C + 7]$ | $[5(S - 1 - F) + 2(S - 1 - F)C + 2]$ |
| Feed stage           | $(5C + 16)$                               | $(2C + 8)$                           |
| $(F - 1) - 1$ stages | $[7(F - 2) + 2(F - 2)C + 2C + 7]$         | $[5(F - 2) + 2(F - 2)C + 2]$         |
| Partial reboiler     | $(3C + 10)$                               | $(2C + 6)$                           |
|                      | $\sum (N_V)_e = 7N + 2NC + 18C + 59$      | $\sum (N_E)_e = 5N + 2NC + 4C + 22$  |

Subtracting  $(C + 3)$  redundant variables for 13 interconnecting streams, according to (5-57), with  $N_A = 0$  (no unspecified repetitions), gives

$$(N_V)_{\text{unit}} = \sum (N_V)_e - 13(C + 3) = 7N + 2NC + 5C + 20$$

Subtracting the corresponding 13 redundant mole-fraction constraints, according to (5-58),

$$(N_E)_{\text{unit}} = \sum (N_E)_e - 13 = 5N + 2NC + 4C + 9$$

Therefore, from (5-60),

$$N_D = (7N + 2NC + 5C + 20) - (5N + 2NC + 4C + 9) = 2N + C + 11$$

Note that the coefficient of  $C$  is only 1, because there is only one feed, and, again, the coefficient of  $N$  is 2.

A set of feasible design variable specifications is:

| Variable Specification  | Number of Variables   |
|---|-----------------------|
| 1. Pressure at each stage (including partial reboiler)            | $N$                   |
| 2. Pressure at reflux divider outlet                              | 1                     |
| 3. Pressure at total condenser outlet                             | 1                     |
| 4. Heat-transfer rate for each stage (excluding partial reboiler) | $(N - 1)$             |
| 5. Heat-transfer rate for divider                                 | 1                     |
| 6. Feed mole fractions and total feed rate                        | $C$                   |
| 7. Feed temperature   | 1                     |
| 8. Feed pressure  | 1                     |
| 9. Condensate temperature (e.g., saturated liquid)                | 1                     |
| 10. Total number of stages, $N$                                   | 1                     |
| 11. Feed stage location   | 1                     |
| 12. Sidestream stage location                                     | 1                     |
| 13. Sidestream total flow rate, $S$                               | 1                     |
| 14. Total distillate flow rate, $D$ or $D/F$                      | 1                     |
| 15. Reflux flow rate, $L_R$ , or reflux ratio, $L_R/D$            | 1                     |
|   | $N_D = (2N + C + 11)$ |

In most separation operations, variables related to feed conditions, stage heat-transfer rates, and stage pressure are known or set. Remaining specifications have proxies, provided that the variables are mathematically independent. Thus, in the above list, the first nine entries are almost always known or specified. Variables 10 to 15, however, have surrogates. Some of these are: Condenser heat duty,  $Q_C$ ; reboiler heat duty,  $Q_R$ ; recovery or mole fraction of one component in bottoms; and recovery or mole fraction of one component in distillate.

Heat duties  $Q_C$  and  $Q_R$  are not good design variables because they are difficult to specify. A specified condenser duty,  $Q_C$ , might result in a temperature that is not realizable. Similarly, it is much easier to calculate  $Q_R$  knowing the total flow rate and enthalpy of the bottom streams than vice versa.  $Q_R$  and  $Q_C$  are so closely related that both should not be specified. Preferably,  $Q_C$  is fixed by distillate rate and reflux ratio, and  $Q_R$  is calculated from the overall energy balance.

Other proxies are possible, but the problem of independence of variables requires careful consideration. Distillate product rate,  $Q_C$ , and  $L_R/D$ , for example, are not independent. It should also be noted that if recoveries of more than two key species are specified, the result can be nonconvergence of the computations because the specified composition may not exist at equilibrium.

As an alternative to the solution to Example 5.4, the degrees of freedom for the unit of Figure 5.19 can be determined quickly by modifying a similar unit in Table 5.4.

## SUMMARY

1. A cascade is a collection of stages arranged to: (a) accomplish a separation not achievable in a single stage, and/or (b) reduce the amount of mass- or energy-separating agent.
2. Cascades are single- or multiple-sectioned and configured in cocurrent, crosscurrent, or countercurrent arrays. Cascades are readily computed if equations are linear in component split ratios.
3. Equation (5-10) gives stage requirements for countercurrent solid-liquid leaching and/or washing involving constant underflow and mass transfer of one component.
4. Stages required for single-section, liquid-liquid extraction with constant distribution coefficients and immiscible solvent and carrier are given by (5-19), (5-22), and (5-29) for, respectively, cocurrent, crosscurrent, and (the most efficient) countercurrent flow.
5. Single-section stage requirements for a countercurrent cascade for absorption and stripping can be estimated with the Kremser equations, (5-48), (5-50), (5-54), and (5-55). Such cascades are limited in their ability to achieve high degrees of separation.

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## STUDY QUESTIONS

- 5.1. What is a separation cascade? What is a hybrid system?
- 5.2. What is the difference between a countercurrent and a crosscurrent cascade?

The closest unit is (b), which differs from that in Figure 5.19 by only a sidestream. From Table 5.3, an equilibrium stage with heat transfer but without a sidestream (f) has  $N_D = (2C + 6)$ , while an equilibrium stage with heat transfer and a sidestream (h) has  $N_D = (2C + 7)$ , or one additional degree of freedom. When this sidestream stage is in a cascade, an additional degree of freedom is added for its location. Thus, two degrees of freedom are added to  $N_D = 2N + C + 9$  for unit operation (b) in Table 5.4. The result is  $N_D = 2N + C + 11$ , which is identical to that determined in Example 5.4.

In a similar manner, the above example can be readily modified to include a second feed stage. By comparing values for elements (f) and (g) in Table 5.3, we see that a feed adds  $C + 2$  degrees of freedom. In addition, one more degree of freedom must be added for the location of this feed stage in a cascade. Thus, a total of  $C + 3$  degrees of freedom are added, giving  $N_D = 2N + 2C + 14$ .

6. A two-section, countercurrent cascade can achieve a sharp split between two key components. The top (rectifying) section purifies the light components and increases recovery of heavy components. The bottom (stripping) section provides the opposite functions.
7. Equilibrium cascade equations involve parameters referred to as washing  $W$ , extraction  $E$ , absorption  $A$ , and stripping  $S$  factors and distribution coefficients, such as  $K$ ,  $K_D$ , and  $R$ , and phase flow ratios, such as  $S/F$  and  $L/V$ .
8. Single-section membrane cascades increase purity of one product and recovery of the main component in that product.
9. Hybrid systems may reduce energy expenditures and make possible separations that are otherwise difficult, and/or improve the degree of separation.
10. The number of degrees of freedom (number of specifications) for a mathematical model of a cascade is the difference between the number of variables and the number of independent equations relating those equations. For a single-section, countercurrent cascade, the recovery of one component can be specified. For a two-section, countercurrent cascade, two recoveries can be specified.

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- 5.3. What is the limitation of a single-section cascade? Does a two-section cascade overcome this limitation?
- 5.4. What is an interlinked system of stages?

- 5.5. Which is more efficient, a crosscurrent cascade or a counter-current cascade?
- 5.6. Under what conditions can a countercurrent cascade achieve complete extraction?
- 5.7. Why is a two-section cascade used for distillation?
- 5.8. What is a group method of calculation?
- 5.9. What is the Kremser method? To what type of separation operations is it applicable? What are the major assumptions of the method?
- 5.10. What is an absorption factor? What is a stripping factor?
- 5.11. In distillation, what is meant by reflux, boilup, rectification section, and stripping section?

- 5.12. Under what conditions is a membrane cascade of multiple stages in series necessary?
- 5.13. Why are hybrid systems often considered?
- 5.14. Give an example of a hybrid system that involves recycle.
- 5.15. Explain how a distillation–crystallization hybrid system works for a binary mixture that exhibits both an azeotrope and a eutectic.
- 5.16. When solving a separation problem, are the number and kind of specifications obvious? If not, how can the required number of specifications be determined?
- 5.17. Can the degrees of freedom be determined for a hybrid system? If so, what is the easiest way to do it?

## EXERCISES

### Section 5.1

#### 5.1. Interlinked cascade arrangement.

Devise an interlinked cascade like Figure 5.2e, but with three columns for separating a four-component feed into four products.

#### 5.2. Batchwise extraction process.

A liquid–liquid extraction process is conducted batchwise as shown in Figure 5.20. The process begins in Vessel 1 (Original), where 100 mg each of solutes A and B are dissolved in 100 mL of water. After adding 100 mL of an organic solvent that is more selective for A than B, the distribution of A and B becomes that shown for Equilibration 1 with Vessel 1. The organic-rich phase is

transferred to Vessel 2 (Transfer), leaving the water-rich phase in Vessel 1 (Transfer). The water and the organic are immiscible. Next, 100 mL of water is added to Vessel 2, resulting in the phase distribution shown for Vessel 2 (Equilibration 2). Also, 100 mL of organic is added to Vessel 1 to give the phase distribution shown for Vessel 1 (Equilibration 2). The batch process is continued by adding Vessel 3 and then 4 to obtain the results shown. (a) Study Figure 5.20 and then draw a corresponding cascade diagram, labeled in a manner similar to Figure 5.2b. (b) Is the process cocurrent, countercurrent, or crosscurrent? (c) Compare the separation with that for a batch equilibrium step. (d) How could the cascade be modified to make it countercurrent? [See O. Post and L.C. Craig, *Anal. Chem.*, **35**, 641 (1963).]

#### 5.3. Two-stage membrane cascade.

Nitrogen is removed from a gas mixture with methane by gas permeation (see Table 1.2) using a glassy polymer membrane that is selective for nitrogen. However, the desired degree of separation cannot be achieved in one stage. Draw sketches of two different two-stage membrane cascades that might be used.

### Section 5.2

#### 5.4. Multistage leaching of oil.

In Example 4.9, 83.25% of the oil is leached by benzene using a single stage. Calculate the percent extraction of oil if: (a) two countercurrent equilibrium stages are used to process 5,000 kg/h of soybean meal with 5,000 kg/h of benzene; (b) three countercurrent stages are used with the flows in part (a). (c) Also determine the number of countercurrent stages required to extract 98% of the oil with a solvent rate twice the minimum.

#### 5.5. Multistage leaching of $\text{Na}_2\text{CO}_3$ .

For Example 5.1, involving the separation of sodium carbonate from an insoluble oxide, compute the minimum solvent feed rate. What is the ratio of actual solvent rate to the minimum solvent rate? Determine and plot the percent recovery of soluble solids with a cascade of five countercurrent equilibrium stages for solvent flow rates from 1.5 to 7.5 times the minimum value.

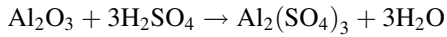
#### 5.6. Production of aluminum sulfate.

Aluminum sulfate (alum) is produced as an aqueous solution from bauxite ore by reaction with aqueous sulfuric acid, followed by three-stage, countercurrent washing to separate soluble aluminum sulfate from the insoluble content of the bauxite, which is then followed by evaporation. In a typical process, 40,000 kg/day of solid bauxite containing 50 wt%  $\text{Al}_2\text{O}_3$  and 50% inert is crushed and fed with the stoichiometric amount of 50 wt% aqueous sulfuric acid to a reactor, where the  $\text{Al}_2\text{O}_3$  is

|         |  |          |        |                 |                 |
|---------|--|----------|--------|-----------------|-----------------|
|         |  | Vessel 1 |        |                 |                 |
| Organic |  |          |        |                 |                 |
| Aqueous |  | 100 A    | 100 B  |                 | Original        |
|         |  |          |        |                 |                 |
| Organic |  | 66.7 A   | 33.3 B |                 |                 |
| Aqueous |  | 33.3 A   | 66.7 B |                 | Equilibration 1 |
|         |  |          |        |                 |                 |
|         |  | Vessel 2 |        |                 |                 |
| Organic |  |          | 66.7 A | 33.3 B          |                 |
| Aqueous |  | 33.3 A   | 66.7 B |                 | Transfer        |
|         |  |          |        |                 |                 |
| Organic |  | 22.2 A   | 22.2 B | 44.4 A          | 11.1 B          |
| Aqueous |  | 11.1 A   | 44.4 B | 22.2 A          | 22.2 B          |
|         |  |          |        | Equilibration 2 |                 |
|         |  | Vessel 3 |        |                 |                 |
| Organic |  |          | 22.2 A | 22.2 B          | 44.4 A          |
| Aqueous |  | 11.1 A   | 44.4 B | 22.2 A          | 22.2 B          |
|         |  |          |        | Transfer        |                 |
|         |  |          |        |                 |                 |
| Organic |  | 7.4 A    | 14.8 B | 29.6 A          | 14.8 B          |
| Aqueous |  | 3.7 A    | 29.6 B | 14.8 A          | 7.4 B           |
|         |  |          |        | Equilibration 3 |                 |
|         |  | Vessel 4 |        |                 |                 |
| Organic |  |          | 7.4 A  | 14.8 B          | 29.6 A          |
| Aqueous |  | 3.7 A    | 29.6 B | 14.8 A          | 7.4 B           |
|         |  |          |        | Transfer        |                 |
|         |  |          |        |                 |                 |
| Organic |  | 2.5 A    | 9.9 B  | 14.8 A          | 7.4 B           |
| Aqueous |  | 1.2 A    | 19.7 B | 7.4 A           | 29.6 B          |
|         |  |          |        | Equilibration 4 |                 |

Figure 5.20 Liquid–liquid extraction process for Exercise 5.2.

reacted completely to alum by:



The slurry from the reactor (digester), consisting of solid inert material from the ore and an aqueous solution of aluminum sulfate, is then fed to a three-stage, countercurrent washing unit to separate the aqueous aluminum sulfate from the inert material. If the solvent is 240,000 kg/day of water and the underflow from each washing stage is 50 wt% water on a solute-free basis, compute the flows in kg/day of aluminum sulfate, water, and inert solid in the product streams leaving the cascade. What is the recovery of the aluminum sulfate? Would addition of one stage be worthwhile?

### 5.7. Rinse cycle for washing clothes.

(a) When rinsing clothes, would it be more efficient to divide the water and rinse several times, or should one use all the water in one rinse? Explain. (b) Devise a washing machine that gives the most efficient rinse cycle for a fixed amount of water.

## Section 5.3

### 5.8. Batch extraction of acetic acid.

An aqueous acetic acid solution containing 6.0 mol/L of acid is extracted with chloroform at 25°C to recover the acid (B) from chloroform-insoluble impurities in the water. The water (A) and chloroform (C) are immiscible. If 10 L of solution are to be extracted at 25°C, calculate the % extraction of acid obtained with 10 L of chloroform under the following conditions: (a) the entire quantity of solvent in a single batch extraction; (b) three batch extractions with one-third of the solvent in each batch; (c) three batch extractions with 5 L of solvent in the first, 3 L in the second, and 2 L in the third batch.

Assume the distribution coefficient for the acid is  $K''_{DB} = (c_B)_C / (c_B)_A = 2.8$ , where  $(c_B)_C$  = concentration of acid in chloroform and  $(c_B)_A$  = concentration of acid in water, both in mol/L.

### 5.9. Extraction of uranyl nitrate.

A 20 wt% solution of uranyl nitrate (UN) in water is to be treated with tributyl phosphate (TBP) to remove 90% of the uranyl nitrate in batchwise equilibrium contacts. Assuming water and TBP are mutually insoluble, how much TBP is required for 100 g of solution if, at equilibrium, (g UN/g TBP) = 5.5(g UN/g H<sub>2</sub>O) and: (a) all the TBP is used at once in one stage; (b) half is used in each of two consecutive stages; (c) two countercurrent stages are used; (d) an infinite number of crosscurrent stages is used; and (e) an infinite number of countercurrent stages is used?

### 5.10. Extraction of uranyl nitrate.

The uranyl nitrate (UN) in 2 kg of a 20 wt% aqueous solution is extracted with 500 g of tributyl phosphate. Using the equilibrium data in Exercise 5.9, calculate and compare the % recoveries for the following alternative procedures: (a) a single-stage batch extraction; (b) three batch extractions with 1/3 of the total solvent used in each batch (solvent is withdrawn after contacting the entire UN phase); (c) a two-stage, cocurrent extraction; (d) a three-stage, countercurrent extraction; (e) an infinite-stage, countercurrent extraction; and (f) an infinite-stage, crosscurrent extraction.

### 5.11. Extraction of dioxane.

One thousand kg of a 30 wt% dioxane in water solution is to be treated with benzene at 25°C to remove 95% of the dioxane. The benzene is dioxane-free, and the equilibrium data of Example 5.2 applies. Calculate the solvent requirements for: (a) a single batch extraction; (b) two crosscurrent stages using equal amounts of benzene; (c) two countercurrent stages; (d) an infinite number of crosscurrent stages; and (e) an infinite number of countercurrent stages.

### 5.12. Extraction of benzoic acid.

Chloroform is used to extract benzoic acid from wastewater effluent. The benzoic acid is present at a concentration of 0.05 mol/L in the effluent, which is discharged at 1,000 L/h. The distribution coefficient for benzoic acid is  $c^I = K_D'' c^{II}$ , where  $K_D'' = 4.2$ ,  $c^I$  = molar concentration of solute in solvent, and  $c^{II}$  = molar concentration of solute in water. Chloroform and water may be assumed immiscible. If 500 L/h of chloroform is to be used, compare the fraction benzoic acid removed in: (a) a single equilibrium contact; (b) three crosscurrent contacts with equal portions of chloroform; and (c) three countercurrent contacts.

### 5.13. Extraction of benzoic acid.

Repeat Example 5.2 with a solvent for  $E = 0.90$ . Display your results in a plot like Figure 5.7. Does countercurrent flow still have a marked advantage over crosscurrent flow? Is it desirable to choose the solvent and solvent rate so that  $E > 1$ ? Explain.

### 5.14. Extraction of citric acid from a broth.

A clarified broth from fermentation of sucrose using *Aspergillus niger* consists of 16.94 wt% citric acid, 82.69 wt% water, and 0.37 wt% other solutes. To recover citric acid, the broth would normally be treated first with calcium hydroxide to neutralize the acid and precipitate it as calcium citrate, and then with sulfuric acid to convert calcium citrate back to citric acid. To avoid the need for calcium hydroxide and sulfuric acid, U.S. Patent 4,251,671 describes a solvent-extraction process using N,N-diethyldodecanamide, which is insoluble in water and has a density of 0.847 g/cm<sup>3</sup>. In a typical experiment at 30°C, 50 g of 20 wt% citric acid and 80 wt% water was contacted with 0.85 g of amide. The resulting organic phase, assumed to be in equilibrium with the aqueous phase, contained 6.39 wt% citric acid and 2.97 wt% water. Determine: (a) the partition (distribution) coefficients for citric acid and water, and (b) the solvent flow rate in kg/h needed to extract 98% of the citric acid in 1,300 kg/h of broth using five countercurrent, equilibrium stages, with the partition coefficients from part (a), but ignoring the solubility of water in the organic phase. In addition, (c) propose a series of subsequent steps to produce near-pure citric acid crystals. In part (b), how serious would it be to ignore the solubility of water in the organic phase?

### 5.15. Extraction of citric acid from a broth.

A clarified broth of 1,300 kg/h from the fermentation of sucrose using *Aspergillus niger* consists of 16.94 wt% citric acid, 82.69 wt% water, and 0.37 wt% other solutes. To avoid the need for calcium hydroxide and sulfuric acid in recovering citric acid from clarified broths, U.S. Patent 5,426,220 describes a solvent-extraction process using a mixed solvent of 56% tridodecyl lauryl amine, 6% octanol, and 38% aromatics-free kerosene, which is insoluble in water. In one experiment at 50°C, 570 g/min of 17 wt% citric acid in a fermentation liquor from pure carbohydrates was contacted in five countercurrent stages with 740 g/minute of the mixed solvent. The result was 98.4% extraction of citric acid. Determine: (a) the average partition (distribution) coefficient for citric acid from the experimental data, and (b) the solvent flow rate in kg/h needed to extract 98% of the citric acid in the 1,300 kg/h of clarified broth using three countercurrent, equilibrium stages, with the partition coefficient from part (a).

## Section 5.4

### 5.16. Multicomponent, multistage absorption.

(a) Repeat Example 5.3 for  $N = 1, 3, 10$ , and 30 stages. Plot the % absorption of each of the five hydrocarbons and the total feed gas, as well as % stripping of the oil versus the number of stages,  $N$ . Discuss your results. (b) Solve Example 5.3 for an absorbent flow

rate of 330 lbmol/h and three theoretical stages. Compare your results to those of Example 5.3. What is the effect of trading stages for absorbent?

### 5.17. Minimum absorbent flow.

Estimate the minimum absorbent flow rate required for the separation in Example 5.3 assuming the key component is propane, whose exit flow rate in the vapor is to be 155.4 lbmol/hr.

### 5.18. Isothermal, multistage absorption.

Solve Example 5.3 with the addition of a heat exchanger at each stage so as to maintain isothermal operation of the absorber at: (a) 125°F and (b) 150°F. What is the effect of temperature on absorption in this range?

### 5.19. Multicomponent, multistage absorption.

One million lbmol/day of a gas of the composition below is absorbed by *n*-heptane at -30°F and 550 psia in an absorber with 10 theoretical stages so as to absorb 50% of the ethane. Calculate the required flow rate of absorbent and the distribution, in lbmol/h, of all components between the exiting gas and liquid.

| Component | Mole Percent in Feed Gas | <i>K</i> -value @ -30°F and 550 psia |
|-----------|--------------------------|--------------------------------------|
| $C_1$     | 94.9                     | 2.85                                 |
| $C_2$     | 4.2                      | 0.36                                 |
| $C_3$     | 0.7                      | 0.066                                |
| $nC_4$    | 0.1                      | 0.017                                |
| $nC_5$    | 0.1                      | 0.004                                |

### 5.20. Multistage stripper.

A stripper at 50 psia with three equilibrium stages strips 1,000 kmol/h of liquid at 300°F with the following molar composition: 0.03%  $C_1$ , 0.22%  $C_2$ , 1.82%  $C_3$ , 4.47%  $nC_4$ , 8.59%  $nC_5$ , 84.87%  $nC_{10}$ . The stripping agent is 1,000 kmol/h of superheated steam at 300°F and 50 psia. Use the Kremser equation to estimate the compositions and flow rates of the stripped liquid and exiting rich gas. Assume a *K*-value for  $C_{10}$  of 0.20 and that no steam is absorbed. Calculate the dew-point temperature of the exiting gas at 50 psia. If it is above 300°F, what can be done?

## Section 5.7

### 5.21. Degrees of freedom for reboiler and condenser.

Verify the values given in Table 5.3 for  $N_V$ ,  $N_E$ , and  $N_D$  for a partial reboiler and a total condenser.

### 5.22. Degrees of freedom for mixer and divider.

Verify the values given in Table 5.3 for  $N_V$ ,  $N_E$ , and  $N_D$  for a stream mixer and a stream divider.

### 5.23. Specifications for a distillation column.

Maleic anhydride with 10% benzoic acid is a byproduct of the manufacture of phthalic anhydride. The mixture is to be distilled in a column with a total condenser and a partial reboiler at a pressure of 13.2 kPa with a reflux ratio of 1.2 times the minimum value to give a product of 99.5 mol% maleic anhydride and a bottoms of 0.5 mol% anhydride. Is this problem completely specified?

### 5.24. Degrees of freedom for distillation.

Verify  $N_D$  for the following unit operations in Table 5.4: (b), (c), and (g). How would  $N_D$  change if two feeds were used?

### 5.25. Degrees of freedom for absorber and stripper.

Verify  $N_D$  for unit operations (e) and (f) in Table 5.4. How would  $N_D$  change if a vapor sidestream were pulled off some stage located between the feed stage and the bottom stage?

### 5.26. Degrees of freedom for extractive distillation.

Verify  $N_D$  for unit operation (h) in Table 5.4. How would  $N_D$  change if a liquid sidestream was added to a stage that was located between the feed stage and stage 2?

### 5.27. Design variables for distillation.

The following are not listed as design variables for the distillation operations in Table 5.4: (a) condenser heat duty; (b) stage temperature; (c) intermediate-stage vapor rate; and (d) reboiler heat load. Under what conditions might these become design variables? If so, which variables listed in Table 5.4 could be eliminated?

### 5.28. Degrees of freedom for condenser change.

For distillation, show that if a total condenser is replaced by a partial condenser, the number of degrees of freedom is reduced by 3, provided the distillate is removed solely as a vapor.

### 5.29. Replacement of a reboiler with live steam.

Unit operation (b) in Table 5.4 is heated by injecting steam into the bottom plate of the column, instead of by a reboiler, for the separation of ethanol and water. Assuming a fixed feed, an adiabatic operation, 1 atm, and a product alcohol concentration: (a) What is the total number of design variables for the general configuration? (b) How many design variables are needed to complete the design? Which variables do you recommend?

### 5.30. Degrees-of-freedom for a distillation column.

(a) For the distillation column shown in Figure 5.21, determine the number of independent design variables. (b) It is suggested that a feed of 30% A, 20% B, and 50% C, all in moles, at 37.8°C and 689 kPa, be processed in the unit of Figure 5.21, with 15-plates in a 3-m-diameter column, which operates at vapor velocities of 0.3 m/s and an *L/V* of 1.2. The pressure drop per plate is 373 Pa, and the condenser is cooled by plant water at 15.6°C.

The product specifications in terms of the concentration of A in the distillate and C in the bottoms have been set by the process department, and the plant manager has asked you to specify a feed rate for the column. Write a memorandum to the plant manager pointing out why you can't do this, and suggest alternatives.

### 5.31. Degrees of freedom for multistage evaporation.

Calculate the number of degrees of freedom for the mixed-feed, triple-effect evaporator system shown in Figure 5.22. Assume that the steam and all drain streams are at saturated conditions and that the feed is an aqueous solution of a dissolved organic solid. Also, assume all overhead streams are pure steam. If this evaporator system is used to concentrate a feed containing 2 wt% dissolved organic to a product with 25 wt% dissolved organic, using 689-kPa saturated steam, calculate the number of unspecified design variables and suggest likely candidates. Assume perfect insulation against heat loss.

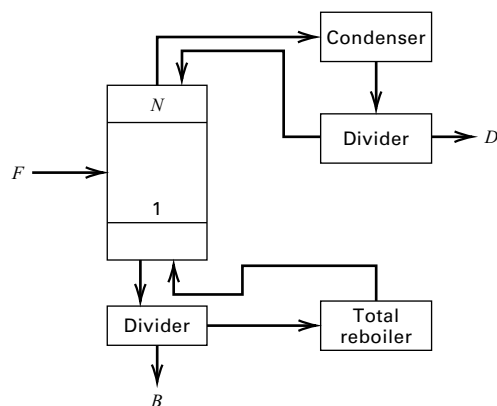


Figure 5.21 Conditions for Exercise 5.30.

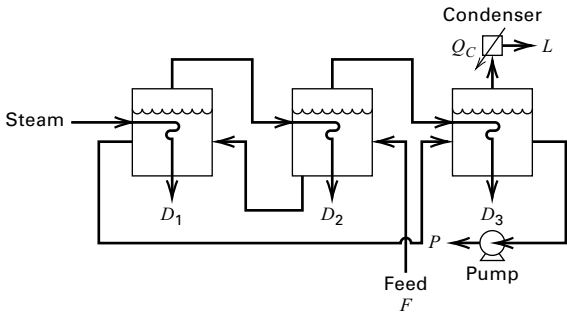


Figure 5.22 Conditions for Exercise 5.31.

**5.32. Degrees of freedom for a reboiled stripper.**

A reboiled stripper, shown in Figure 5.23, is to be designed. Determine: (a) the number of variables; (b) the number of equations relating the variables; and (c) the number of degrees of freedom. Also indicate (d) which additional variables, if any, need to be specified.

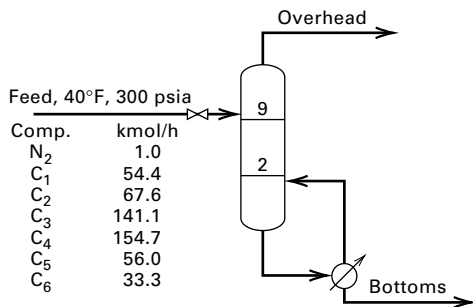


Figure 5.23 Conditions for Exercise 5.32.

**5.33. Degrees of freedom of a thermally coupled distillation system.**

The thermally coupled distillation system in Figure 5.24 separates a mixture of three components. Determine: (a) the number of

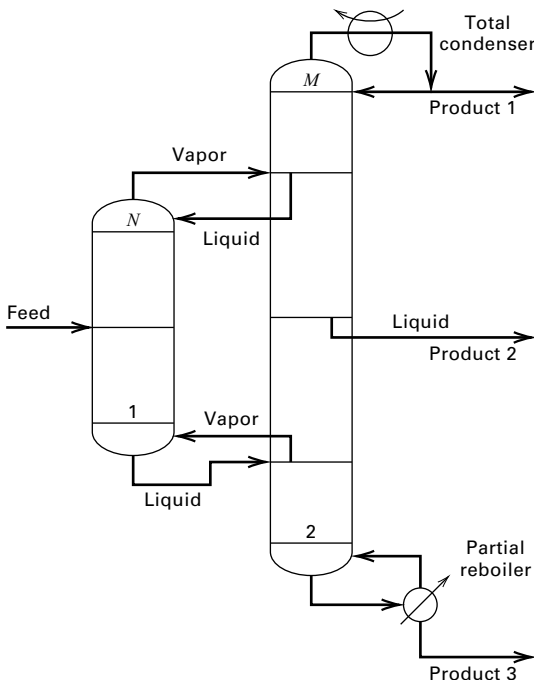


Figure 5.24 Conditions for Exercise 5.33.

variables; (b) the number of equations relating the variables; and (c) the number of degrees of freedom. Also propose (d) a reasonable set of design variables.

**5.34. Adding a pasteurization section to distillation column.**

When feed to a distillation column contains impurities that are much more volatile than the desired distillate, it is possible to separate the volatile impurities from the distillate by removing the distillate as a liquid sidestream from a stage several stages below the top. As shown in Figure 5.25, this additional section of stages is referred to as a pasteurizing section. (a) Determine the number of degrees of freedom for the unit. (b) Determine a reasonable set of design variables.

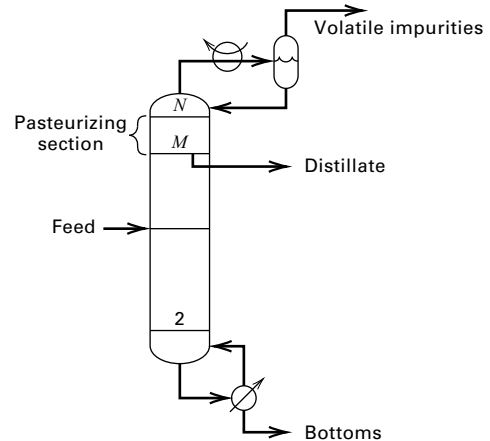


Figure 5.25 Conditions for Exercise 5.34.

**5.35. Degrees of freedom for a two-column system.**

A system for separating a feed into three products is shown in Figure 5.26. Determine: (a) the number of variables; (b) the number of equations relating the variables; and (c) the number of degrees of freedom. Also propose (d) a reasonable set of design variables.

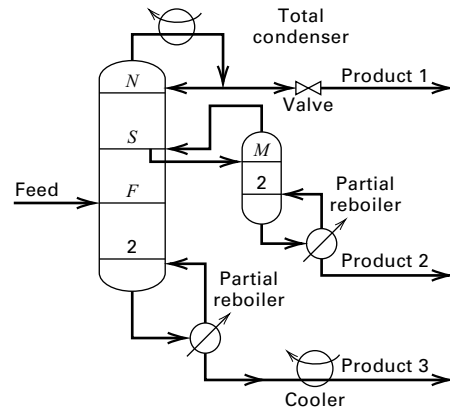


Figure 5.26 Conditions for Exercise 5.35.

**5.36. Design variables for an extractive distillation.**

A system for separating a binary mixture by extractive distillation, followed by ordinary distillation for recovery and recycle of the solvent, is shown in Figure 5.27. Are the design variables shown sufficient to specify the problem completely? If not, what additional design variable(s) should be selected?

**5.37. Design variables for a three-product distillation column.**

A single distillation column for separating a three-component mixture into three products is shown in Figure 5.28. Are the design variables shown sufficient to specify the problem completely? If not, what additional design variable(s) would you select?



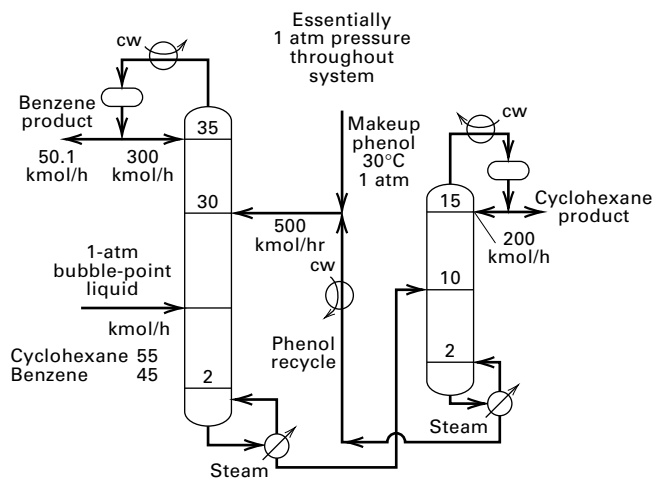


Figure 5.27 Conditions for Exercise 5.36.

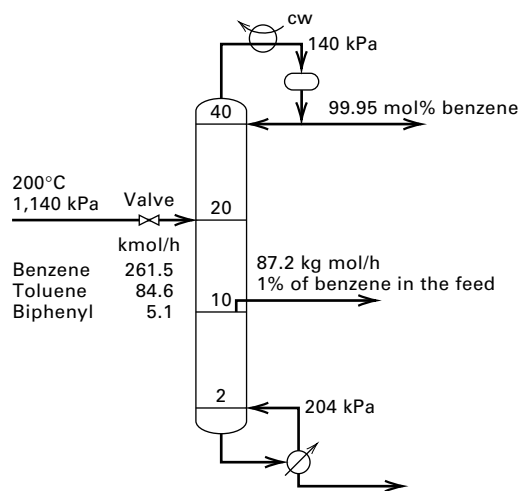


Figure 5.28 Conditions for Exercise 5.37.