

K -values and enthalpies estimated from the P-R equation of state, the following results are obtained:

Component	kmol/h		
	Feed 120°F 485 psia	Vapor 112°F 165 psia	Liquid 112°F 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

This case involves a wide-boiling feed, so the procedure involving (4-17) is the best choice. The above results show that only a small amount of vapor ($\Psi = 0.0035$), predominantly H_2 and CH_4 , is produced by the adiabatic flash. The computed 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 can differ as to the extent of solubility of the three components in each of the two liquid phases. The simplest case is shown in Figure 4.13a, 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. In this case, the equations can be derived for a single equilibrium stage, using the variables F , S , $L^{(1)}$, and $L^{(2)}$ to refer, respectively, to the flow rates (or amounts) of the feed, solvent, exiting extract, and exiting raffinate. By definition, the extract is the exiting liquid phase that contains the solvent and the extracted solute; the raffinate is the exiting liquid phase that contains the carrier, A, of the feed and the portion of the solute, B, that is not extracted. Although the extract is shown in Figure 4.13a as leaving from the top of the stage, this will only be so if the extract is the lighter (lower-density) exiting phase. Assuming that the entering solvent contains no solute, B, it is convenient to write material balance and phase-equilibrium equations for the solute, B. These two equations may be written in terms of molar or mass flow rates. To obtain the simplest result, it is preferable to express

compositions of the solute as mass or mole ratios instead of mass or mole fractions.

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 coefficient defined in terms of mass or mole ratios. Substituting (4-22) into (4-21) to eliminate $X_B^{(E)}$ gives

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

It is convenient to define an extraction factor, E_B , for the solute B:

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

The larger the value of E , the greater the extent to which the solute is extracted. Large values of E result from large values of the distribution coefficient, K'_{D_B} , or large ratios of solvent to carrier. Substituting (4-24) in (4-23) gives the fraction of B that is not extracted as

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

where it is clear that the larger the extraction factor, the smaller the fraction of B not extracted.

Values of 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_i} , in terms of ratios, are related to K_{D_i} in terms of fractions as given in (2-20) by

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

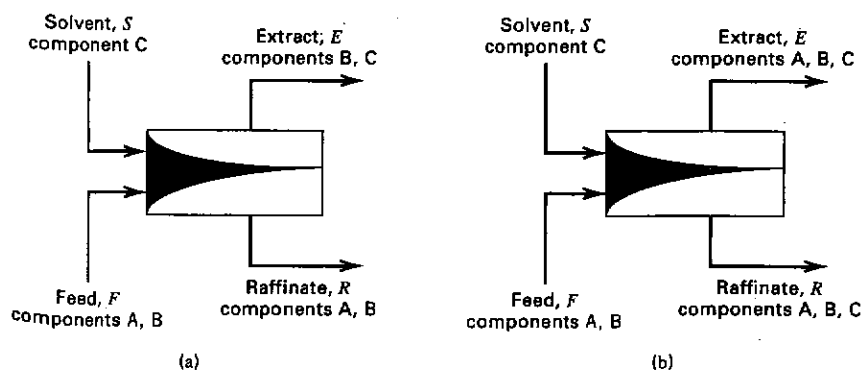


Figure 4.13 Phase splitting of ternary mixtures: (a) components A and C mutually insoluble; (b) components A and C partially soluble.

When values of x_i are small, K'_D approaches K_D . As discussed in Chapter 2, the distribution coefficient, K_D , which can be determined from activity coefficients using the expression $K_{D_B} = \gamma_B^{(2)}/\gamma_B^{(1)}$ when mole fractions are used, is a strong function of equilibrium-phase compositions and temperature. However, when the raffinate and extract are both dilute in the solute, activity coefficients of the solute can be approximated by the values at infinite dilution so that K_{D_B} can be taken as a constant at a given temperature. An extensive listing of such K_{D_B} values in mass fraction units for various ternary systems is given in *Perry's 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 4.5

A feed of 13,500 kg/h consists of 8 wt% acetic acid (B) in water (A). The removal of the acetic acid is to be accomplished by liquid-liquid extraction at 25°C with methyl isobutyl ketone solvent (C), because distillation of the feed would require vaporization of large amounts of water. If the raffinate is to contain only 1 wt% acetic acid, estimate the kilograms per hour of solvent required if a single equilibrium stage is used.

SOLUTION

Assume that the carrier (water) and the solvent are immiscible. From *Perry's Handbook*, take $K_D = 0.657$ in mass-fraction units for this system. For the relatively low concentrations of acetic acid in this problem, assume that $K'_D = K_D$.

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

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

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 is a very large solvent flow rate compared to the feed rate—more than a factor of 10! Multiple stages should be used to reduce the solvent rate or a solvent with a larger distribution coefficient should be sought. For 1-butanol as the solvent, $K_D = 1.613$.

In the ternary liquid-liquid system, shown in Figure 4.13b, components A and C are partially soluble in each other and component B again distributes between the extract and raffinate phases. Both of these exiting phases contain all components present in the feed and solvent. This case is by far the most commonly encountered, and a number of different phase diagrams and computational techniques have been

devised to determine the equilibrium compositions. Examples of phase diagrams are shown in Figure 4.14 for the water (A)–ethylene glycol (B)–furfural (C) system at 25°C and a pressure of 101 kPa, which is above the bubble-point pressure, so no vapor phase exists. Experimental data for this system were obtained by Conway and Norton [18]. The pairs water–ethylene glycol and furfural–ethylene glycol are each completely miscible. The only partially miscible pair is furfural–water. Furfural might be used as a solvent to remove the solute, ethylene glycol, from water; the furfural-rich phase is the extract, and the water-rich phase is the raffinate.

Figure 4.14a, an equilateral-triangular diagram, is the most common display of ternary liquid-liquid equilibrium data in the chemical literature. Any point located within or on an edge of the triangle represents a mixture composition. Such a diagram has the property that the sum of the lengths of the perpendicular lines drawn from any interior point to the sides equals the altitude of the triangle. Thus, if each of the three altitudes 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 base opposite the pure furfural apex, which represents 100% furfural. Figure 4.14a is constructed for compositions based on mass fractions (mole fractions and volume fractions are also sometimes used). Thus, the point M in Figure 4.14a represents a mixture of feed and solvent (before phase separation) containing 18.9 wt% water, 20 wt% ethylene glycol, and 61.1 wt% furfural.

The miscibility limits for the furfural–water binary system are at D and G. The miscibility boundary (saturation or binodal curve) DEPRG can be obtained experimentally by a *cloud-point titration*; water, for example, is added to a (clear) 50 wt% solution of furfural and glycol, and it is noted that the onset of cloudiness due to the formation of a second phase occurs when the mixture is 11% water, 44.5% furfural, and 44.5% glycol by weight. Other miscibility data are given in Table 4.5, from which the miscibility curve in Figure 4.14a was drawn.

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

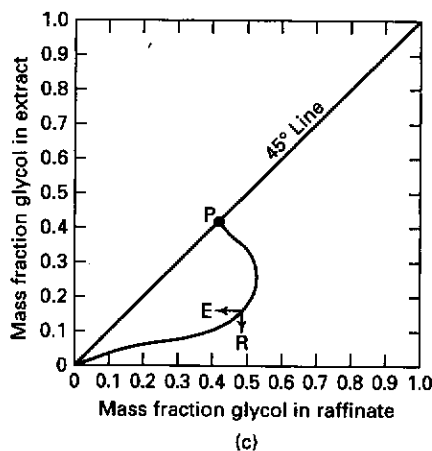
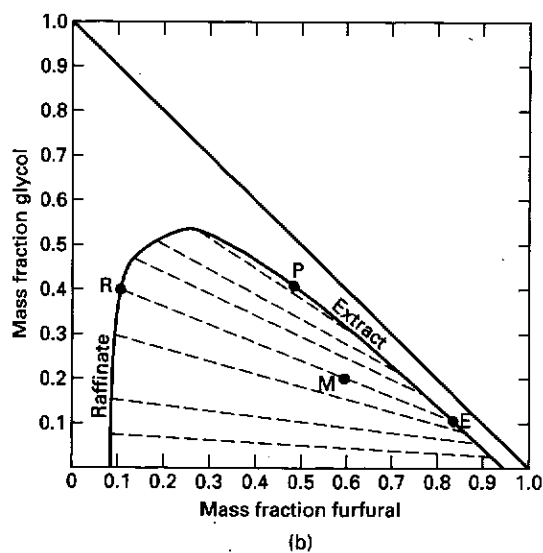
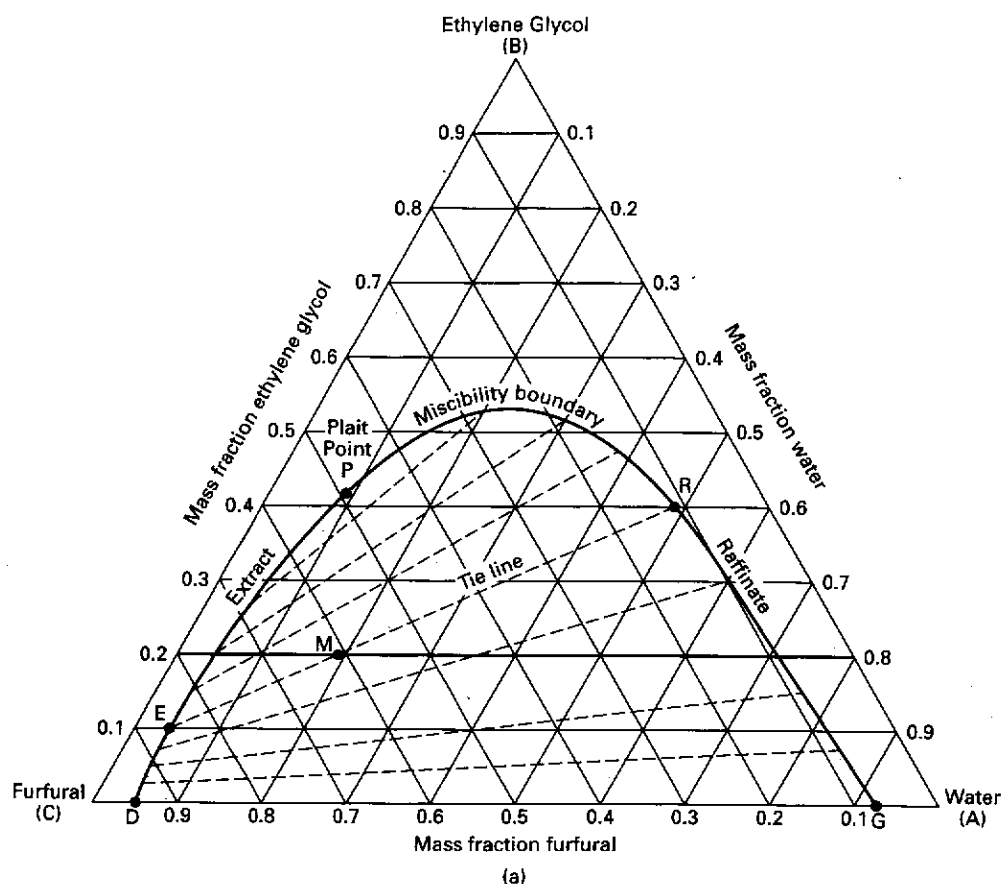


Figure 4.14 Liquid-liquid equilibrium, ethylene glycol-furfural-water, 25°C, 101 kPa: (a) equilateral triangular diagram; (b) right triangular diagram; (c) equilibrium solute diagram in mass fractions (*continues*).

Tie lines, shown as dashed lines below the miscibility boundary in Figure 4.14a, are used to connect points on the miscibility boundary, DEPRG, that represent equilibrium-phase compositions. To obtain data to construct tie lines, such as ER, it is necessary to make a mixture such as M (20% glycol, 18.9% water, and 61.1% furfural),

equilibrate it, and then chemically analyze the resulting equilibrium extract and raffinate phases E and R (in this case, 10% glycol, 3.9% water, and 86.1% 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

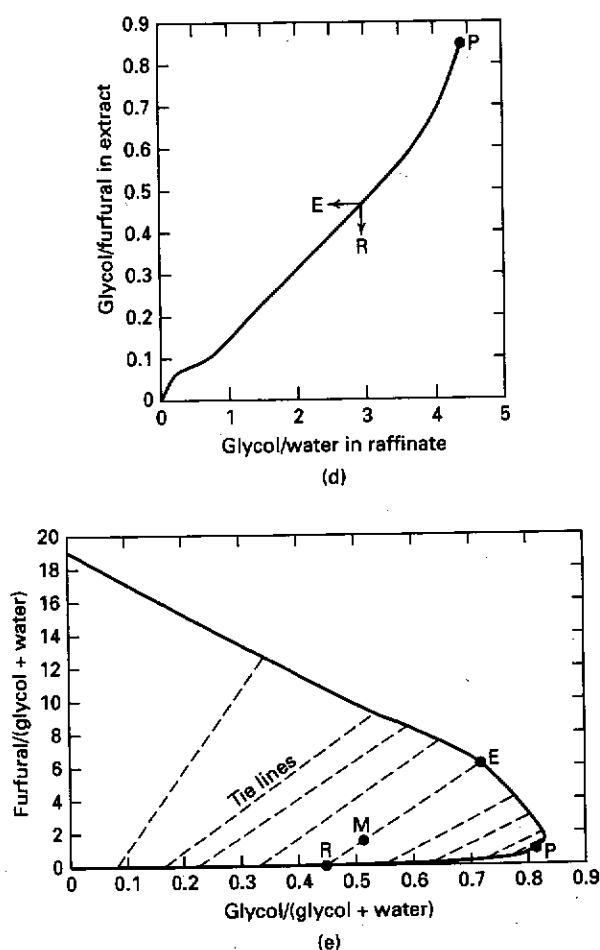


Figure 4.14 (Continued) (d) equilibrium solute diagram in mass ratios; (e) Janecke diagram.

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

to a point and the two phases become one phase. Tie-line data for this system are given in Table 4.6, in terms of glycol composition.

When there is mutual solubility between two phases, the thermodynamic variables necessary to define the equilib-

rium system are temperature, pressure, and the concentrations of the components in each phase. According to the phase rule, (4-1), for a three-component, two-liquid-phase system, there are three degrees of freedom. At constant temperature and pressure, specification of the concentration of one component in either of the phases suffices to completely define the state of the system. Thus, as shown in Figure 4.14a, one value for glycol weight percent on the miscibility boundary curve fixes the composition of the corresponding phase and, by means of the tie line, the composition of the other equilibrium phase.

Figure 4.14b is a representation of the same system on a right-triangular diagram. Here the concentrations in weight percent of any two of the three components (normally the solute and solvent) are given, the concentration of the third being obtained by 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 the computer program, CSpace, which can be downloaded from the web site at www.ugr.es/~cspace.

Figures 4.14c and 4.14d are representations of the same ternary system in terms of weight fraction and weight ratios of the solute, respectively. Figure 4.14c is simply a plot of the equilibrium (tie-line) data of Table 4.6 in terms of solute mass fraction. In Figure 4.14d, 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 4.14c, a nearly straight line is often evident near the origin, where the slope is the distribution coefficient, K_D , for the solute at infinite dilution.

In 1906, Janecke [10] suggested the equilibrium data display shown as Figure 4.14e. Here, the mass of solvent per unit mass of solvent-free material, furfural/(water + glycol), is plotted as the ordinate versus the mass ratio, on a solvent-free basis, of glycol/(water + glycol) as abscissa. The ordinate and abscissa apply to both phases. Equilibrium conditions are related by tie lines. Mole ratios can be used also to construct Janecke diagrams.

Any of the five diagrams in Figure 4.14 can be used for solving problems involving material balances subject to liquid–liquid equilibrium constraints, as is demonstrated in the following example.

EXAMPLE 4.14
Determine the composition of the equilibrium extract and raffinate phases produced when a 45% by weight glycol (B)–55% 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 4.14, if possible.

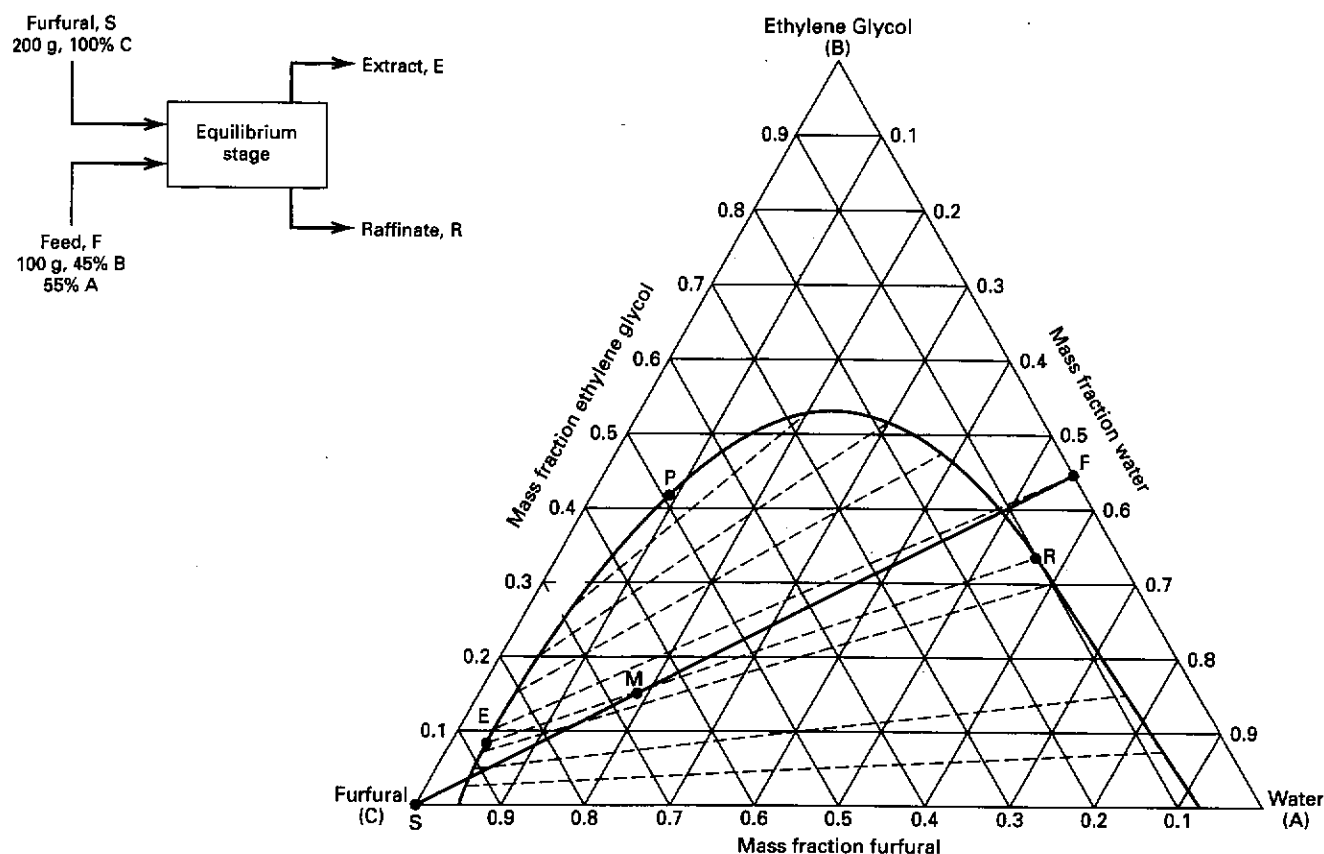


Figure 4.15 Solution to Example 4.7a.

SOLUTION

Assume a basis of 100 g of 45% glycol–water feed. Thus, in Figure 4.13b, the feed (F) is 55 g of A and 45 g of B. The solvent (S) is 200 g of C. Let E = the extract, and R = the raffinate.

(a) By an equilateral-triangular diagram, Figure 4.15:

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

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

Step 3. Apply the inverse-lever-arm rule to the equilateral-triangular phase-equilibrium diagram. Let $w_i^{(1)}$ be the mass fraction of species i in the extract, $w_i^{(2)}$ be the mass fraction of species i in the raffinate, and $w_i^{(M)}$ be the mass fraction of species i in the combined feed and solvent phases.

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

Therefore,

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

Thus, points S , M , and F lie on a straight line, 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.

Step 4. Since M lies in the two-phase region, the mixture must separate along an interpolated dash-dot tie line into the 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 $E = M(RM/ER)$. Because $M = 100 + 200 = 300$ g, and from measurements of the line segments, $E = 300(147/200) = 220$ g and $R = M - E = 300 - 220 = 80$ g.

(b) By a right-triangular diagram, Figure 4.16:

Step 1. Locate the points 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 an equilibrium solute diagram, Figure 4.14c. 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 4.14c 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.

Step 1. Guess a value for $w_B^{(E)}$ and read the equilibrium value, $w_B^{(R)}$, from Figure 4.14c.

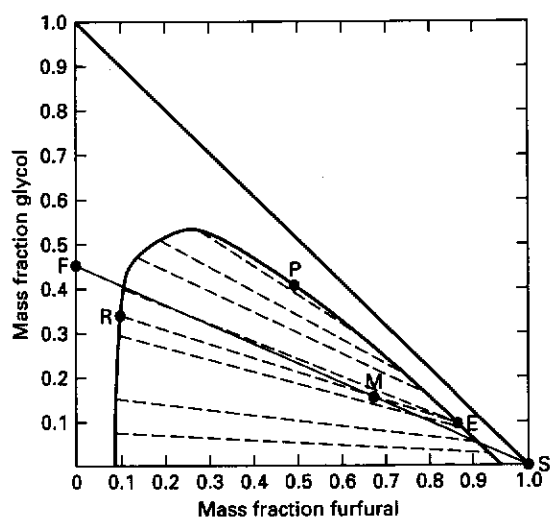


Figure 4.16 Solution to Example 4.7b.

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 equilibrium data from Figures 4.14a, 4.14b, or 4.14e. If not, repeat steps 1 to 3 with a new guess for $w_B^{(E)}$. This procedure leads to the same results obtained in parts (a) and (b).

(d) By an equilibrium solute diagram in mass fractions, Figure 4.14d: This plot suffers from the same limitations as Figure 4.13c in that a solution must be achieved by an iterative procedure.

(e) By a Janecke diagram, Figure 4.17:

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.

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

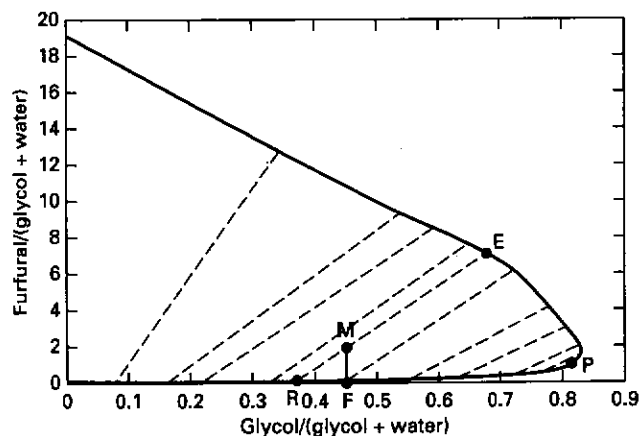


Figure 4.17 Solution to Example 4.7e.

balances apply:

$$\text{Furfural: } 7.1Z^E + 0.10Z^R = 200$$

$$\text{Glycol: } 0.67Z^E + 0.37Z^R = 45$$

Solving these two simultaneous equations, we obtain $Z^E = 27$ g, $Z^R = 73$ g.

Thus, the furfural in the extract = $(7.1)(27 \text{ g}) = 192$ g, the furfural in the raffinate = $200 - 192 = 8$ g, the glycol in the extract = $(0.67)(27 \text{ g}) = 18$ 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. The total extract is $192 + 27 = 219$ g, which is close to the results obtained in 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 the ratio of R/E on a solvent-free basis.

In Figure 4.14, 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 are also common. Figure 4.18 shows examples, taken from Francis [11] and Findlay [12], of four different cases where two pairs of components are only partially soluble.

In Figure 4.18a, two separate two-phase regions are formed, while in Figure 4.18c, in addition to the two-phase regions, a three-phase region, RST, is formed. In Figure 4.18b, the two separate two-phase regions merge. For a ternary mixture, as temperature is reduced, phase behavior may progress from Figure 4.18a to 4.18b to 4.18c. In Figures 4.18a, 4.18b, and 4.18c, all tie lines slope in the same direction. In some systems of importance, *solutropy*, a reversal of tie-line slopes, occurs.

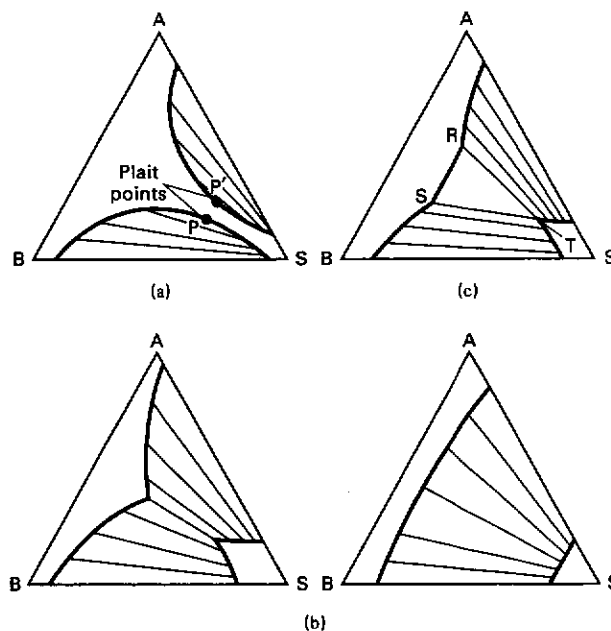


Figure 4.18 Equilibria for 3/2 systems: (a) miscibility boundaries are separate; (b) miscibility boundaries and tie-line equilibria merge; (c) tie lines do not merge and the three-phase region RST is formed.