For example, at 250°C the polymers will be mutually soluble only for PS concentrations less than 0.096 mole fraction or greater than 0.913 mole fraction. Thus the two polymers can be commingled for recycling only in limited proportions. ∎

So far we have considered liquid-liquid equilibrium only for binary mixtures. We next consider multicomponent mixtures. When two solvents are partially miscible (rather than immiscible), their mutual solubility will be affected by the addition of a third component. In this case the equilibrium conditions are

$$\bar{f}_i^I(T, P, \underline{x}^I) = \bar{f}_i^{II}(T, P, \underline{x}^{II}) \tag{11.2-23}$$

or, if an activity coefficient model is used,

$$x_i^I \gamma_i(T, P, \underline{x}^I) = x_i^{II} \gamma_i(T, P, \underline{x}^{II}) \tag{11.2-2}$$

for each of the species i noting that the addition of a third component affects the activity coefficients of all species in the mixture. (In writing these equations we have assumed the existence of only two liquid phases. It is left to the reader to generalize these equations for three coexisting liquid phases.) Thus, the addition of a third component may increase or decrease the equilibrium solubility of the two initially partially miscible solvents. An increase in solubility of this type is termed **salting in** and a decrease **salting out** (see Fig. 11.2-8).[11] In some cases the addition of a solute (usually an electrolyte) can so increase the mutual solubility of two partially miscible fluids that a completely miscible mixture is formed.

A typical liquid-liquid equilibrium problem is to determine the amounts and compositions of the two or more phases that are formed when known amounts of several chemicals are mixed. The equations to be solved are the equilibrium conditions of Eqs. 11.2-2 and the mass balances

$$N_i = N_i^I + N_i^{II} \tag{11.2-24}$$

Thus to compute the equilibrium state when N_1 moles of species 1, N_2 moles of species 2, and so on, are mixed, Eqs. 11.2-2 and 11.2-24 are to be solved. These equations can be difficult to solve, first because of the complicated dependence of the activity coefficients on the mole fractions (these equations are nonlinear) and second, because even in the simplest case of a ternary mixture, there are six coupled equations to be solved. This is best done on a computer with equation-solving software.

A difficulty that arises if there are more than two components is how to graphically represent the phase behavior. Figures can be drawn for a ternary system, either in triangular form (in which the compositions of all three components are represented) or in rectangular form for two of the components, with the composition of the third species obtained by difference.

Ternary systems and triangular diagrams

Figure 11.2-7 is an example of the triangular diagram method of the two-dimensional representation of the three composition variables, and is interpreted as follows. The three apexes of the triangle each represent a pure species. The composition (which, depending on the figure, may be either mass fraction or mole fraction) of each species in a mixture decreases linearly with distance along the perpendicular bisector from the apex for that species to the opposite side of the triangle. Thus each side of the

---

[11] Usually the terms *salting in* and *salting out* are used to describe the increase or decrease in solubility that results from the addition of a salt or electrolyte to a solute-solvent system. Their use here to describe the effects of the addition of a nonelectrolyte is a slight generalization of the definition of these terms.
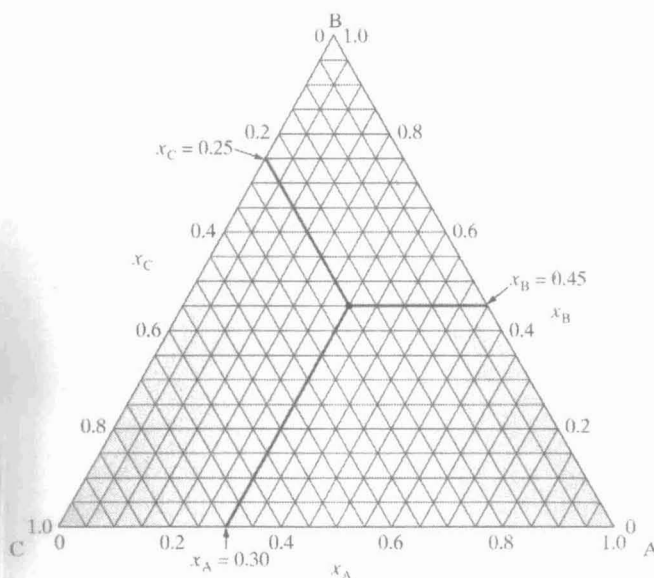
Figure 11.2-7 Triangular diagram representation of the compositions of a ternary mixture in two dimensions.

triangle is a binary mixture lacking the species at the opposite apex (i.e., the bottom of Fig. 11.2-7 represents an A+C binary mixture, the right side mixtures of A+B, and the left side B+C mixtures). For convenience, the fractional concentrations are usually indicated along one side of the triangle for each species.

The fractional concentration of each species at a specific point on the diagram is found by drawing a line through that point parallel to the side opposite the apex for that substance and noting the intersection of this line with the appropriate side of the triangle. This is illustrated in Fig. 11.2-7, where the filled point has the composition $x_A = 0.30$, $x_B = 0.45$, and $x_C = 0.25$, and the lines indicate how these compositions are to be read on this diagram.

A simple example of the use of a triangular diagram is given in the illustration that follows.

ILLUSTRATION 11.2-7
Mass Balance Calculation on a Triangular Diagram

One kilogram of a binary mixture containing 50 wt % of species A and 50 wt % of species B is mixed with two kilograms of a ternary mixture containing 15 wt % of A, 5 wt % of B, and 80 wt % of species C.

a. What is the composition of the final mixture (assuming there is no liquid-liquid phase splitting)?
b. Plot the compositions of the two initial mixtures and the final mixture on a triangular diagram.

SOLUTION

a. The mass balance on each species is
   A: $0.5 \times 1 + 0.15 \times 2 = 0.8$ kg

B: $0.5 \times 1 + 0.05 \times 2 = 0.6$ kg

C: $0.0 \times 1 + 0.80 \times 2 = 1.7$ kg
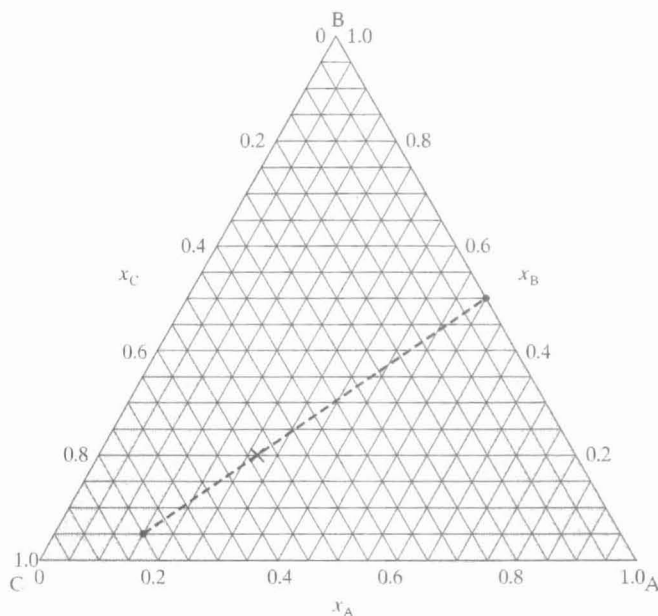
Since, from an overall mass balance, there are 3 kg in the final mixture, the final composition is

A: $0.8/3 = 0.267$ weight fraction or 26.7 wt %

B: $0.6/3 = 0.200$ weight fraction or 20.0 wt %

C: $1.6/3 = 0.533$ weight fraction or 53.3 wt %

b. The two feed compositions and the final mixture composition are plotted on the accompanying triangular diagram.

COMMENT

The final mixture composition is on a straight line connecting the two feed compositions. This is another example of the lever rule, and is merely a result of the mass balances being linear equations. Note also that the composition of the final mixture is found at two-thirds of the distance from the first feed to the second feed in accordance with their relative amounts. This graphical linear relation between the two feeds and the final mixture is the opposite case to that of a single feed that splits into two equilibrium streams, which is the case in liquid-liquid extraction. ∎

The liquid-liquid phase equilibrium data for the methyl isobutyl ketone (MIK) + acetone (A) + water (W) ternary mixture is shown Fig. 11.2-8. The inside of the dome-shaped region in this figure is a region of compositions in which liquid-liquid phase separation occurs, and tie lines are sometimes drawn within the phase separation region (as in this figure) to indicate the compositions of the coexisting phases. (As we will see shortly, phase diagrams can be more complicated than the one shown here.) From the intersection of the two-phase region with the base of the triangular diagram, we see that water and MIK are only slightly soluble in each other, while the binary mixtures of water + acetone and MIK + acetone are mutually soluble and so form only a single
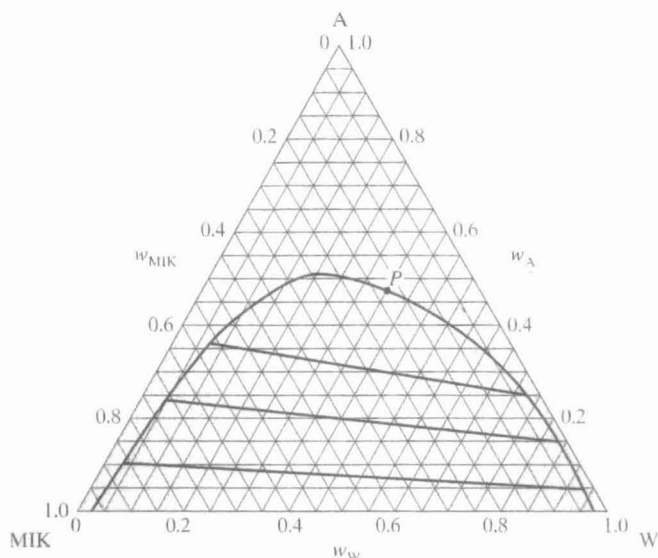
Figure 11.2-8 Liquid-liquid equilibrium compositions in weight fractions for the MIK + acetone + water system at 298.15 K.

liquid phase at all compositions. Note that there is a ternary composition at which the equilibrium tie line is of zero length, and the two equilibrium phases have the same composition. This composition is known as the **plait point** of the mixture and is indicated by the point labeled P in the figure.

Experimental liquid-liquid equilibrium data may be available as complete lists of the composition of each phase, so that triangular diagrams such as the one shown here can easily be prepared. However, it is also common for experimental data to be obtained in a less complete way that requires fewer chemical analyses. For example, if species A and B are mutually soluble, a mixture of a specified composition is prepared (gravimetrically, that is, by weighing each component before mixing), and then small weighed amounts of species C are added (and the solution mixed) until just enough of C has been added for the solution to become cloudy, indicating the formation of a second liquid phase. In this way the composition of the ternary mixture at one point of the liquid-liquid equilibrium (or binodal) curve is obtained without the need to do a chemical analysis. However, the composition of the coexisting equilibrium phase (that is, the other end of the tie line) is not known. (Note that the liquid-liquid equilibrium, or binodal, curve is also referred to as the cloud point curve, a name that is appropriate to the way it was determined. The cloud point curve in liquid-liquid equilibrium is analogous to the dew point or bubble point curve in vapor-liquid equilibrium in that it represents the saturation of a single phase and the formation of a second phase. The new phase is a second liquid at the cloud point, a vapor at the bubble point or a liquid at the dew point.)

The following data for the system methyl isobutyl ketone (MIK)–acetone–water[12] are an example of such data. These data form the boundary of the dome-shaped liquid-liquid coexistence region that was plotted in the triangular diagram of Fig. 11.2-8.

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[12]D. F. Othmer, R. E. White, and E. Trueger, *Ind. Eng. Chem.*, vol. 33, 1240 (1941).

| MIK (wt %)	Acetone (wt %)	Water (wt %)	MIK (wt %)	Acetone (wt %)	Water (wt %)
93.2	4.60	2.33	27.4	48.4	24.1
77.3	18.95	3.86	20.1	46.3	33.5
71.0	24.4	4.66	2.12	3.73	94.2
65.5	28.9	5.53	3.23	20.9	75.8
54.7	37.6	7.82	5.01	30.9	64.2
46.2	43.2	10.7	12.4	42.7	45.0
38.3	47.0	14.8	20.5	46.6	32.8
32.8	48.3	18.8	25.9	50.7	23.4

In addition to these data, usually several two-phase mixtures, with appreciable amounts of the second phase, are prepared and the solute composition measured. Such data for the acetone in the MIK + acetone + water system at 298.15 K are given in the following table

Acetone (wt %) in MIK layer	Acetone (wt %) in water layer
10.66	5.58
18.0	11.83
25.5	15.35
30.5	20.6
35.3	23.8

These data are plotted in Fig. 11.2-9.

The data in Fig. 11.2-9 are used to add the tie lines in Fig. 11.2-8. The procedure is as follows.

1. A composition of the solute, acetone, is arbitrarily chosen for one of the phases—for example, 5 wt % in the water-rich phase. The point at which there is 5 wt % acetone on the water-rich portion of the binodal curve is identified in Fig. 11.2-8. This is one end of a tie line.
2. The acetone composition in the MIK-rich phase in equilibrium with 5 wt % acetone in the water-rich phase is found from Fig. 11.2-9 to be approximately 10 wt %.
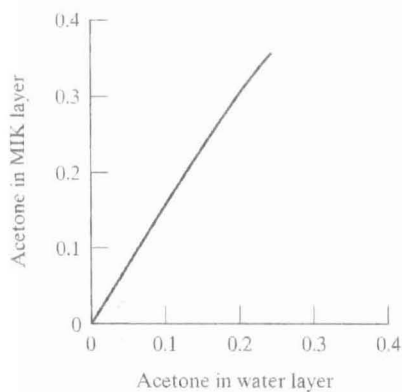

Figure 11.2-9 Distribution of acetone between the coexisting liquid phases in the MIK + acetone + water system at 298.15 K.

3. The point at which there is 10 wt % acetone on the MIK-rich portion of the binodal curve is identified in Fig. 11.2-8. This is the other end of the tie line.
4. The tie line connecting these two points is drawn in Figure 11.2-8.
5. This procedure is repeated for as many other tie lines as are desired.

Note that in this way the complete liquid-liquid equilibrium curve and the tie lines have been obtained with very few chemical analyses. In particular, the binodal curve was obtained gravimetrically, which is generally more accurate than chemical analysis, and the tie lines were obtained for only a few mixtures, and then only by analyzing for the solute (here acetone), and not for all three components in the mixture.

Since only two of the mole fractions or weight fractions are independent in a ternary system (since the three fractions must sum to unity), another way of presenting ternary liquid-liquid equilibrium data is as shown in Fig. 11.2-10 for the MIK + acetone + water system, in which only the MIK and acetone concentrations are presented, and the user must determine the water concentration by difference.

Triangular diagrams and other means of presenting ternary liquid-liquid equilibrium data can be used to design liquid-liquid extraction processes. Such applications are considered elsewhere in the chemical engineering curriculum. However, a brief introduction is given in the two illustrations that follow.
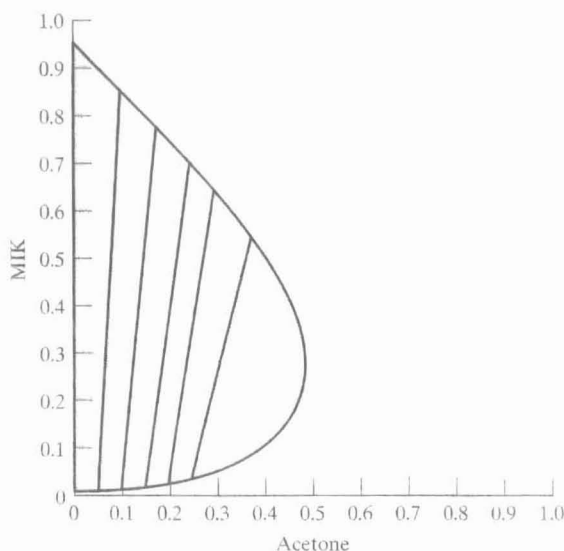
Figure 11.2-10 Liquid-liquid phase diagram for the MIK + acetone + water system at 298.15 K showing only the MIK and acetone weight fractions; the water weight fraction is obtained by difference.

ILLUSTRATION 11.2-8

Liquid-Liquid Extraction of an Organic Chemical from Aqueous Solution

It is desired to remove some of the acetone from a mixture that contains 60 wt % acetone and 40 wt % water by extraction with methyl isobutyl ketone (MIK). If 3 kg of MIK are contacted with 1 kg of the acetone-water mixture, what will be the amounts and compositions of the equilibrium phases?

SOLUTION

This problem is solved using the triangular diagram of Fig. 11.2-8. First the concentration of the combined streams is determined. It consists of 3 kg of MIK, 0.6×1 kg $= 0.6$ kg of acetone, and 0.4×1 kg of water. So the overall feed is 75 wt % MIK, 15 wt % acetone, and 10 wt % water. This point is located on the triangular diagram for this system, and is found to be in the two-liquid phase region. Next, a tie line is drawn through this feed point (indicated by the dashed line in the accompanying figure), and the compositions of the two coexisting phases are found at the two intersections of the tie line with the binodal curve. These compositions are given below.

	MIK (wt %)	Acetone (wt %)	Water (wt %)
MIK-rich	80.5	15.5	4.0
Water-rich	2.0	8.0	90.0
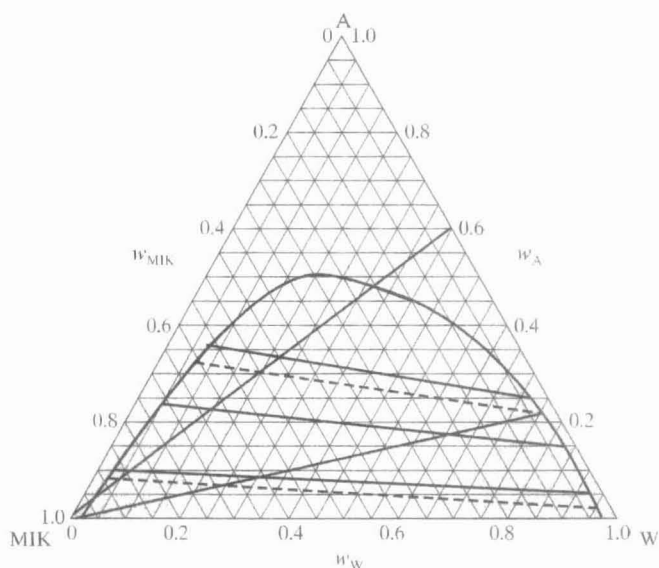
Next, from an overall mass balance,

$$L^{I} + L^{II} = 4 \text{ kg} \quad \text{so that} \quad L^{II} = 4 - L^{I}$$

and a mass balance on any one of the species, say water, we have

$$0.04 \times L^{I} + 0.90 \times L^{II} = 0.04 \times L^{I} + 0.90 \times (4 - L^{I}) = 0.4 \times 1 = 0.4 \text{ kg}$$

which has the solution $L^{I} = 3.721$ and $L^{II} = 0.279$ kg. So by liquid-liquid extraction, we have

	MIK (kg)	Acetone (kg)	Water (kg)
MIK-rich	2.979	0.574	0.148
Water-rich	0.005	0.024	0.27

COMMENT

By this single liquid-liquid extraction step we have been able to remove most of the acetone from the water. However, a great deal of methyl isobutyl ketone has been used. Consequently, this would not be a very useful way to recover acetone from aqueous solution. To reduce the amount

of solvent used, an alternative would be to use a number of stages, each with a smaller amount of pure solvent. Such multistage extractions are frequently done in the chemistry laboratory. This is shown in the next illustration. ∎

ILLUSTRATION 11.2-9

Staged Liquid-Liquid Extraction of an Organic Chemical from Aqueous Solution

The acetone-water mixture of the previous illustration is to be treated by a two-stage extraction with methyl isobutyl ketone (MIK). In the first stage 1 kg of MIK is contacted with 1 kg of the acetone-water mixture. The water-rich phase will go to a second stage, where it will be contacted with another 1 kg of pure MIK. What will be the amounts and compositions of the equilibrium phases at the exit of each stage?

SOLUTION

As in the previous illustration, this problem is solved using the triangular diagram of Fig. 11.2-8. First the concentration of the combined streams in stage 1 is determined. It consists of 1 kg MIK, 0.6×1 kg $= 0.6$ kg acetone, and 0.4×1 kg water. So the overall feed is 50 wt % MIK, 30 wt % acetone, and 20 wt % water. This point is located on the triangular diagram for this system, and found to be in the two-liquid phase region. Following the procedure used in the previous illustration, the compositions of the two phases are as follows.

	MIK (wt %)	Acetone (wt %)	Water (wt %)
MIK-rich	62	32	6
Water-rich	2	23	75
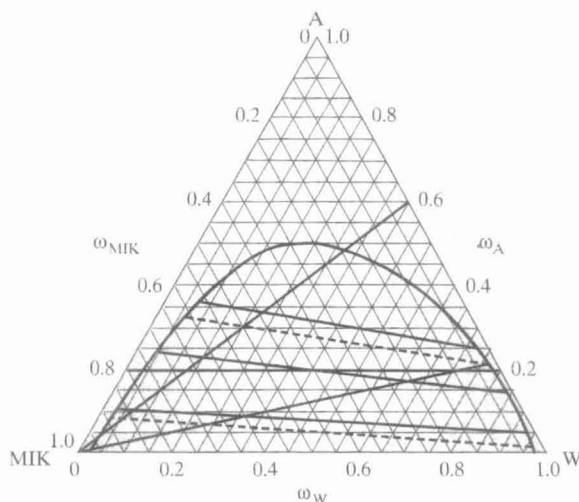
Next, from an overall mass balance,

$$L^{\mathrm{I}} + L^{\mathrm{II}} = 2 \text{ kg} \quad \text{so} \quad L^{\mathrm{II}} = 2 - L^{\mathrm{I}}$$

and a mass balance on water, we have

$$0.06 \times L^{\mathrm{I}} + 0.75 \times L^{\mathrm{II}} = 0.06 \times L^{\mathrm{I}} + 0.75 \times (2 - L^{\mathrm{I}}) = 0.4 \times 1 = 0.4 \text{ kg}$$

which has the solution $L^{\mathrm{I}} = 1.59$ and $L^{\mathrm{II}} = 0.41$ kg.

The feed to the second stage is the following: MIK $= 1 + 0.02 \times 0.41 = 1.008$ kg, acetone $= 0.23 \times 0.41 = 0.094$ kg, and water $= 0.75 \times 0.41 = 0.308$ kg, for a total of 1.41 kg. Therefore, the composition of the combined feed to the second stage is 71.5 wt % MIK, 6.7 wt % acetone, and 21.8 wt % water, which is also in the two-phase region.

Using the tie line through this new feed point, we obtain the following:

	MIK (wt %)	Acetone (wt %)	Water (wt %)
MIK-rich	88.4	7.6	4
Water-rich	2	3	95

From the mass balances $L^{\mathrm{I}} = 1.134$ and $L^{\mathrm{II}} = 0.276$ kg., the water-rich stream leaving the second stage extraction unit contains 0.263 kg water, 0.0083 kg acetone, and 0.0055 kg MIK.

COMMENT

Note that by using two liquid extraction stages instead of a single stage, more acetone has been extracted (only 0.0083 kg in the exit water-rich stream, compared with 0.022 kg in the single-step process), and only 2 kg MIK have been used (of which 0.0055 kg is lost in the water stream), compared with 3 kg in the single-step process with a comparable MIK loss.

This example suggests that staging with smaller amounts of solvent (here MIK) will produce greater recovery than a single-stage process. However, this would involve greater costs since more equipment is needed. Clearly, a careful analysis, including costs, would be required to design the economically optimal process. In such a design, other extraction configurations would have to be considered, such as the countercurrent extraction process shown below and other, more complicated processes. Such designs are considered in a stagewise operations course elsewhere in the chemical engineering curriculum. The purpose of the illustrations here is merely to show the importance of thermodynamic equilibrium in the design of liquid-liquid extraction processes.
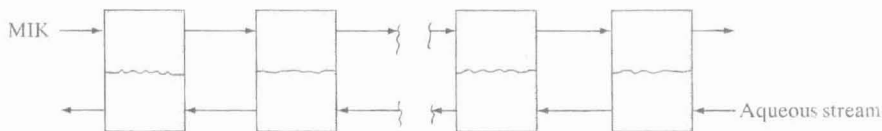
Schematic diagram of a staged liquid-liquid extraction system.

While graphical methods have been used in the illustrations above, that is not what would be done in more careful design, and especially in the design of a chemical process using modern computer simulation software. The procedure would be to use one of the activity coefficient models described in Chapter 9, frequently the NRTL, UNIQUAC, or van Laar model, with parameters adjusted to fit the available liquid-liquid equilibrium data, and solve the equilibrium equations, Eqs. 11.2-2, numerically. This leads to more accurate results than reading numbers from triangular diagrams, as was done in the illustrations here.

In this section we have considered liquid-liquid equilibrium in binary mixtures, and in ternary mixtures in which there was limited mutual solubility between only one pair of components (for example, the methyl isobutyl ketone + water binary mixture in the methyl isobutyl ketone + water + acetone system). In fact, liquid-liquid equilibria can be more complicated than this when two of three binary pairs in a ternary mixture, or all three of the binary pairs, have limited solubility. Such systems can be described by

a generalization of the equations used in this section to allow for three (or more) liquid phases when multicomponent systems are considered:
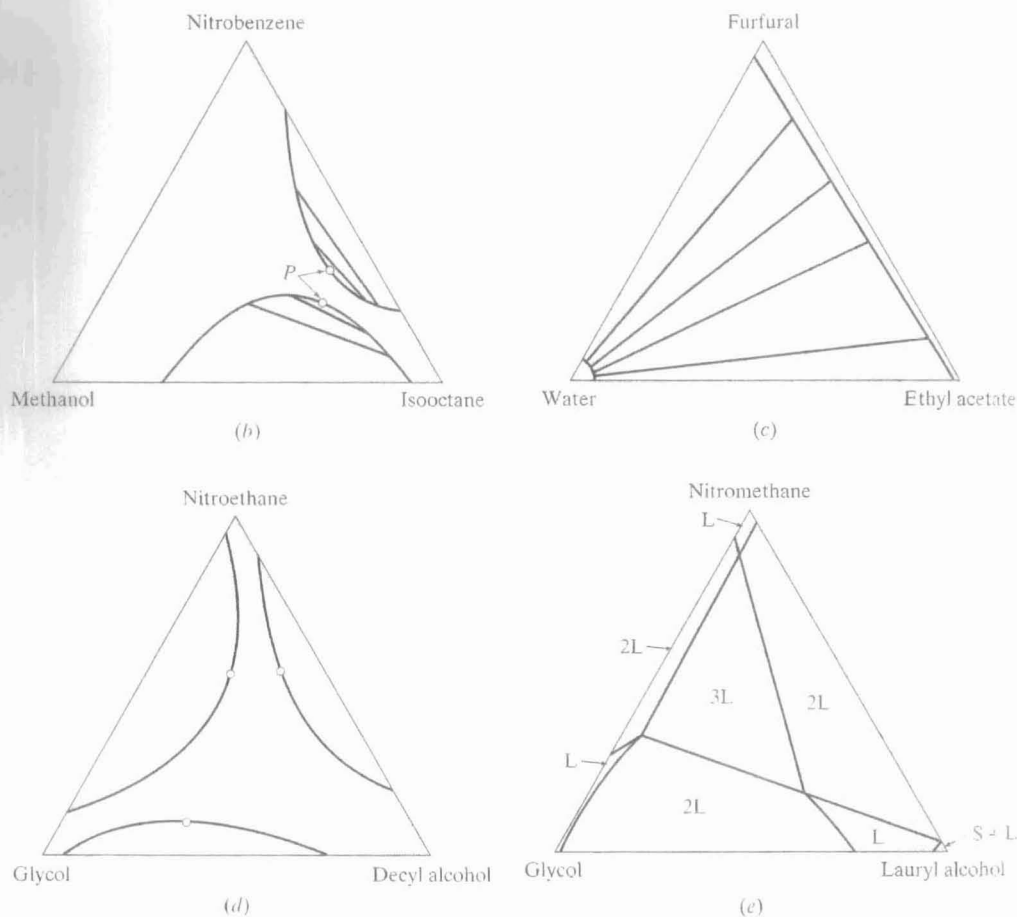
$$x_i^I \gamma_i^I(T, P, \underline{x}^I) = x_i^{II} \gamma_i^{II}(T, P, \underline{x}^{II}) = x_i^{III} \gamma_i^{III}(T, P, \underline{x}^{III}) \quad i = 1, 2, \ldots, \mathcal{C}$$

(11.2-25)

Though we will not analyze such systems here, we conclude this section by showing examples of the types of liquid-liquid equilibria found to occur in ternary mixtures. Figure 11.2-11a is another example of a liquid-liquid phase diagram for a system


(a)
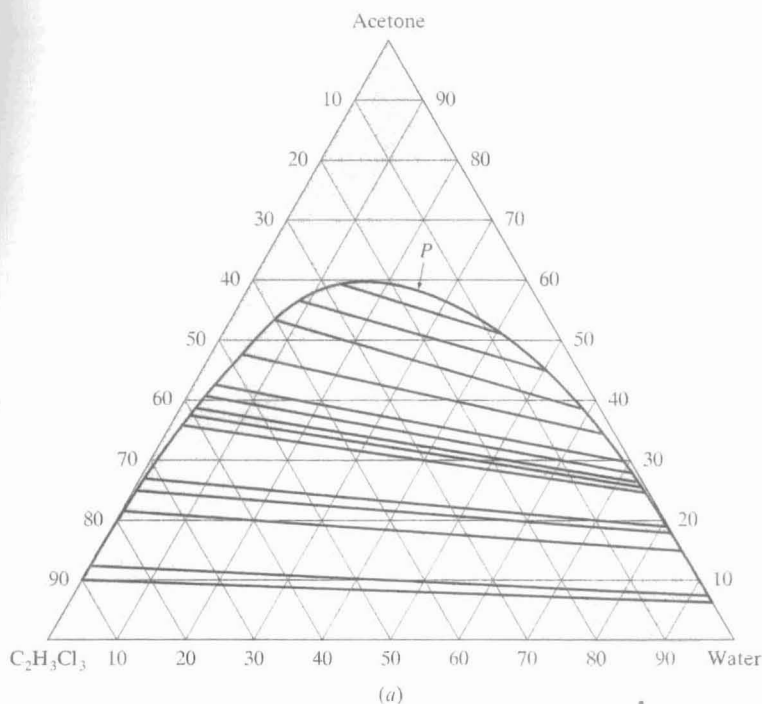
Figure 11.2-11 (a) Equilibrium diagram for the acetone–water–1,1,2-trichloroethane system. [Reprinted with permission from R. E. Treybal, L. D. Weber, and J. F. Daley, *Ind. Eng. Chem.*, **38**, 817 (1946). Copyright by American Chemical Society.] (b) Equilibrium diagram for the nitrobenzene-methanol-isooctane system at 15°C. [Reprinted with permission from A. W. Francis, *Liquid-Liquid Equilibriums*, John Wiley & Sons, New York (1963).] (c) Equilibrium diagram for the furfural–water–ethyl acetate system. [Reprinted with permission from A. W. Francis, *Liquid-Liquid Equilibriums*, John Wiley & Sons, New York (1963).] (d) Equilibrium diagram for the nitroethane–glycol–decyl alcohol system at 10°C. [Reprinted with permission from A. W. Francis, *J. Phys. Chem.*, **60**, 20 (1956). Copyright by the American Chemical Society.] (e) Equilibrium diagram for the nitromethane–glycol–lauryl alcohol system at 20°C, showing the presence of two and three coexisting solid and liquid phases. [Reprinted with permission from A. W. Francis, *J. Phys. Chem.*, **60**, 20 (1956). Copyright by the American Chemical Society.] (f) Equilibrium diagram for carbon dioxide with 10 pairs of other liquids, demonstrating the wide variety of liquid-liquid phase equilibria that occur at 0°C. Note that tie lines and plait points have been included in the diagrams. [Reprinted with permission from A. W. Francis, *J. Phys. Chem.*, **58**, 1099 (1954). Copyright by the American Chemical Society.]

Nitrobenzene

Methanol   Isooctane

(b)

Furfural

Water   Ethyl acetate

(c)

Nitroethane

Glycol   Decyl alcohol

(d)

Nitromethane

Glycol   Lauryl alcohol

(e)

that has a single pair of components that are partially miscible. In the nitrobenzene-methanol-isooctane system of Fig. 11.2-11b, there are 2 two-phase regions, and in the furfural–water–ethyl acetate system of Fig. 11.2-11c the 2 two-phase regions merge into a band. The nitroethane–glycol–decyl alcohol system of Fig. 11.2-11d has three distinct two-phase regions, whereas Fig. 11.2-11e, for the nitromethane–glycol–lauryl alcohol system, shows the merging of these two-phase regions (denoted by $2L$) into regions where three liquid phases coexist (denoted by $3L$).

Figure 11.2-11f, for the liquid-liquid phase equilibrium behavior of liquid carbon dioxide with pairs of other liquids, has been included to illustrate the variety of types of ternary system phase diagrams the chemist and engineer may encounter. Complete discussions of these different types of phase diagrams are given in numerous places (including A. W. Francis, *Liquid-Liquid Equilibriums*, John Wiley & Sons, New York, 1963)

In a ternary mixture there is also the possibility of three or more liquid phases in equilibrium, which is allowed by a generalization of the two-phase equilibrium analysis of this section (see Problem 11.2-1). Indeed, note that some of the phase diagrams in Fig. 11.2-11 show regions of liquid-liquid-liquid equilibrium.

(f)
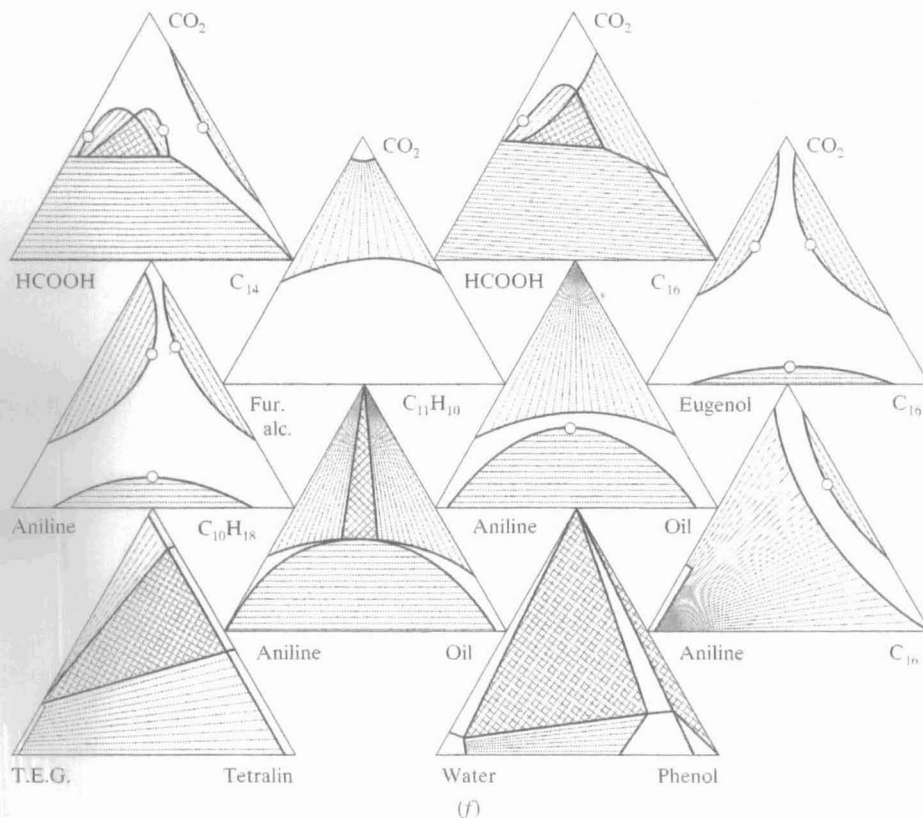
1.2-1 a. Show that if two liquids form a regular solution, the critical temperature for phase separation is

$$RT_c = \frac{2x_1 x_2 \underline{V}_1^2 \underline{V}_2^2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)^3}(\delta_1 - \delta_2)^2 = \frac{2\Phi_1 \Phi_2 \underline{V}_1 \underline{V}_2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)}(\delta_1 - \delta_2)^2$$

**b.** Show that the composition at the upper consolute temperature is

$$x_1 = 1 - x_2 = \frac{(\underline{V}_1^2 + \underline{V}_2^2 - \underline{V}_1 \underline{V}_2)^{1/2} - \underline{V}_1}{\underline{V}_2 - \underline{V}_1}$$

and develop an expression for the upper consolute temperature for the regular solution model.

1.2-2 Following is a portion of a phase diagram for two liquids that are only partially miscible. Note that the phase diagram contains both the coexistence curve (solid line) and a curve indicating the stability limit for each phase (dashed line) (i.e., the bility limit for each phase (dashed line) (i.e., the

dashed line represents the greatest concentration of the dilute species, or extent of supersaturation, that can occur in a metastable phase). This line is called the spinodal curve. For a binary mixture for which $\underline{G}^{ex} = Ax_1 x_2$, develop the equations to be used to

a. Compute the liquid-liquid coexistence line.

b. Compute the spinodal curve.
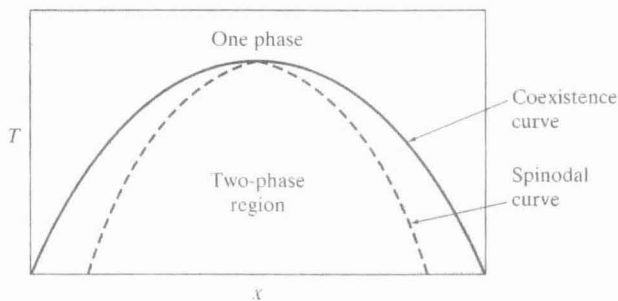
11.2-3 The two figures below have been obtained from measurements of the excess Gibbs energy and ex-