CHAPTER

10

INTRODUCTION TO MULTICOMPONENT SYSTEMS

Gibbs phase rule

$$F = C - P + 2$$

$F = C - P + 2 = 1 - 2 + 2 = 1$ pure fluid

$F = 2 - 2 + 2 = 2$ binary mixture,

the **phase envelope.**

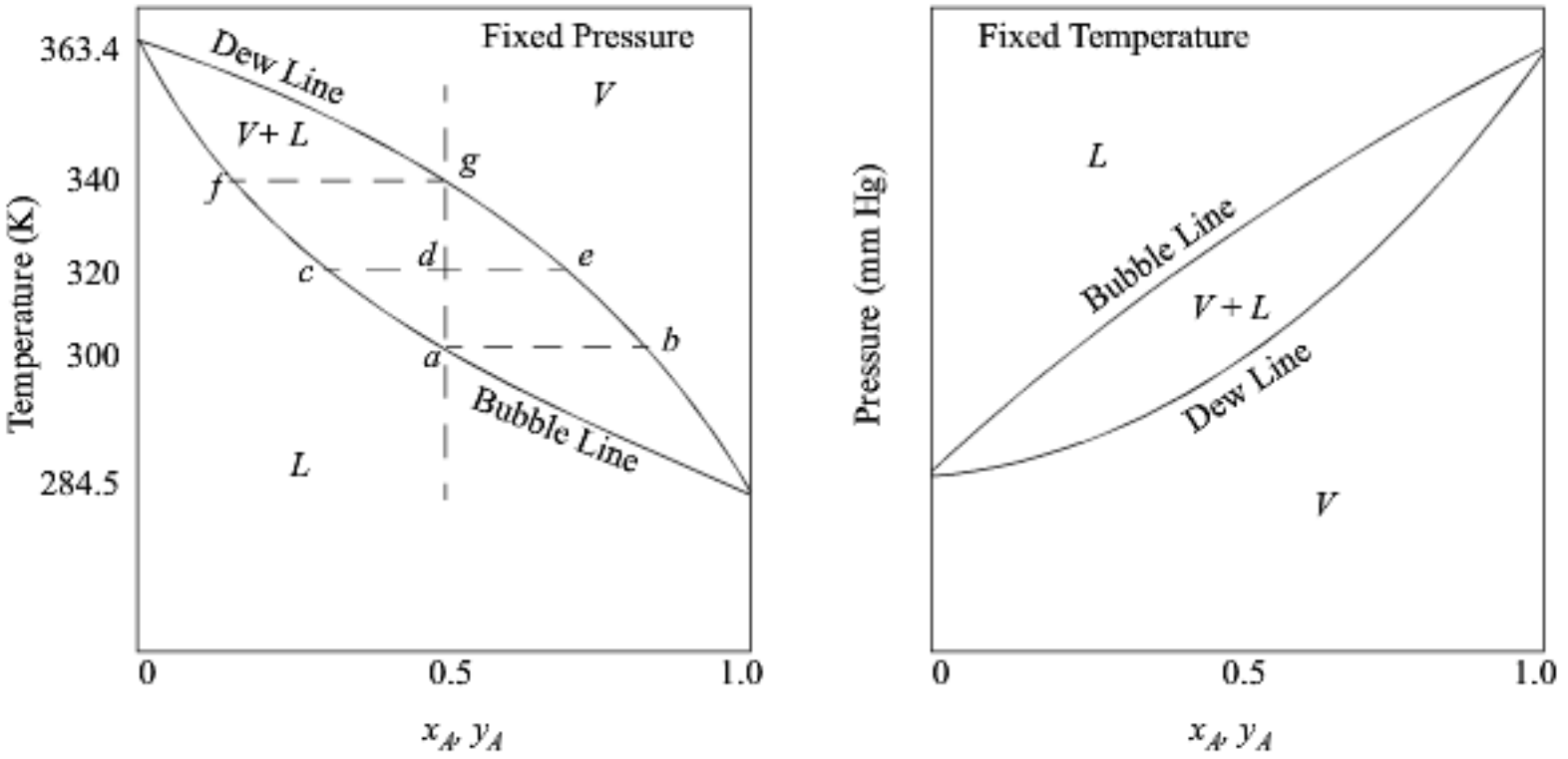

Figure 10.1 *Illustration of T-x-y (left) and P-x-y (right) diagrams.*

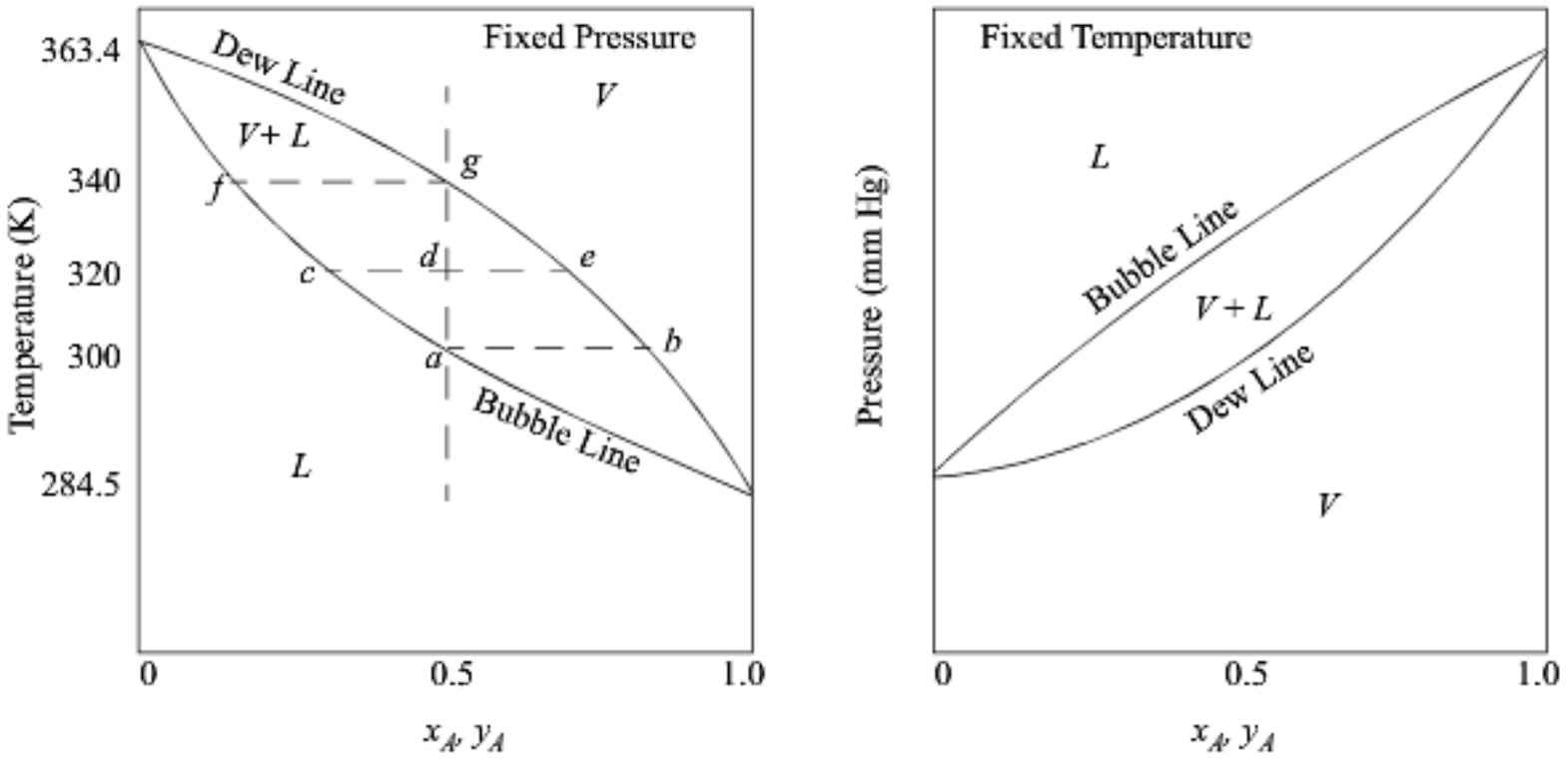

Figure 10.1 *Illustration of T-x-y (left) and P-x-y (right) diagrams.*

lever rule

$$\frac{L}{F} = \frac{z_A - y_A}{x_A - y_A} \qquad 10.1$$

$$\frac{V}{F} = \frac{x_A - z_A}{x_A - y_A} \qquad 10.2$$

10.2 VAPOR-LIQUID EQUILIBRIUM (VLE) CALCULATIONS

bubble-point pressure (BP)

dew-point pressure (DP)

dew-point temperature (DT)

isothermal flash (FL)

adiabatic flash (FA)

Table 10.1 *Summary of the Types of Phase Equilibria Calculations (This Table is Independent of the VLE Model)*

Type	Information known	Information computed	Criteria	Effort
BP	$T, x_i = z_i$	P, y_i	$\sum_i y_i = \sum_i K_i x_i = 1$	Easiest
DP	$T, y_i = z_i$	P, x_i	$\sum_i x_i = \sum_i (y_i / K_i) = 1$	Not bad
BT	$P, x_i = z_i$	T, y_i	$\sum_i y_i = \sum_i K_i x_i = 1$	Difficult
DT	$P, y_i = z_i$	T, x_i	$\sum_i x_i = \sum_i (y_i / K_i) = 1$	Difficult
FL	P, T^{in}, T^{out}, z_i	$x_i, y_i, V/F, Q$	$\sum_i \frac{z_i(1-K_i)}{1_i + (V/F)(K_i - 1)} = 0$, E-bal for Q	Quite difficult
FA	$P, T^{in}, z_i, Q = 0$	$x_i, y_i, V/F, T^{out}$	$\sum_i \frac{z_i(1-K_i)}{1_i + (V/F)(K_i - 1)} = 0$, E-bal	Most difficult

Principles of Calculations

Standard approaches to solving VLE problems utilize the ratio of vapor mole fraction to liquid mole fraction, known as the **VLE *K*-ratio:**

$$K_i \equiv y_i / x_i \qquad 10.3$$

For a bubble calculation, all the x_i are known, and we find the y_i by solving for the condition where $\sum_i y_i = 1$ written in terms of x_i, namely $\sum_i K_i x_i = 1$. For dew calculations, all y_i are known, and we solve for the condition where $\sum_i x_i = 1$ written in terms of y_i and K_i. For a flash calculation, we solve for the condition where $\sum_i x_i - \sum_i y_i = 0$ written in terms of the overall mole fraction z_i and K_i.

Raoult's law (Like a Solution Ideal Gas law)

More Complex EOSs are presented in later chapters

Strategies for Solving VLE Problems

1. Decide if the liquid, vapor, or overall composition is known from the problem statement.
2. Identify if the fluid is at a bubble or dew point. If the fluid is at a bubble point, the overall composition will be the same as the liquid composition. At the dew point, the overall composition will be the same as the vapor.
3. Identify if the P, T, or both P and T are fixed. Decide if the system is adiabatic.
4. The information collected in the first three steps can be used with the second column in Table 10.1 to identify the method.
5. Select a method to calculate the VLE K-ratio.
6. Decide if the method will be iterative, and if so, generate an initial guess for the solution. Approaches for handling iterative calculations are introduced in the following chapters and examples.

Table 10.1 *Summary of the Types of Phase Equilibria Calculations (This Table is Independent of the VLE Model)*

Type	Information known	Information computed	Criteria	Effort
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BT	$P, x_i = z_i$	T, y_i	$\sum_i y_i = \sum_i K_i x_i = 1$	Difficult
DT	$P, y_i = z_i$	T, x_i	$\sum_i x_i = \sum_i (y_i/K_i) = 1$	Difficult
FL	P, T^{in}, T^{out}, z_i	$x_i, y_i, V/F, Q$	$\sum_i \frac{z_i(1-K_i)}{1_i + (V/F)(K_i - 1)} = 0$, E-bal for Q	Quite difficult
FA	$P, T^{in}, z_i, Q = 0$	$x_i, y_i, V/F, T^{out}$	$\sum_i \frac{z_i(1-K_i)}{1_i + (V/F)(K_i - 1)} = 0$, E-bal	Most difficult

Iterative Calculations

When the *K*-ratios vary, VLE calculations require iterative solutions from an initial guess. For performing iterative calculations, useful aids include the Solver tool of Excel or the `fzero()` or `fsolve()` function of MATLAB. Many of the following examples summarize detailed calculations to illustrate fully the iterative procedure. In practice, the detailed calculations can be performed rapidly using a solver. Online supplements summarize the use of the iterative aids and the methods for successive substitution.

10.3 BINARY VLE USING RAOULT'S LAW

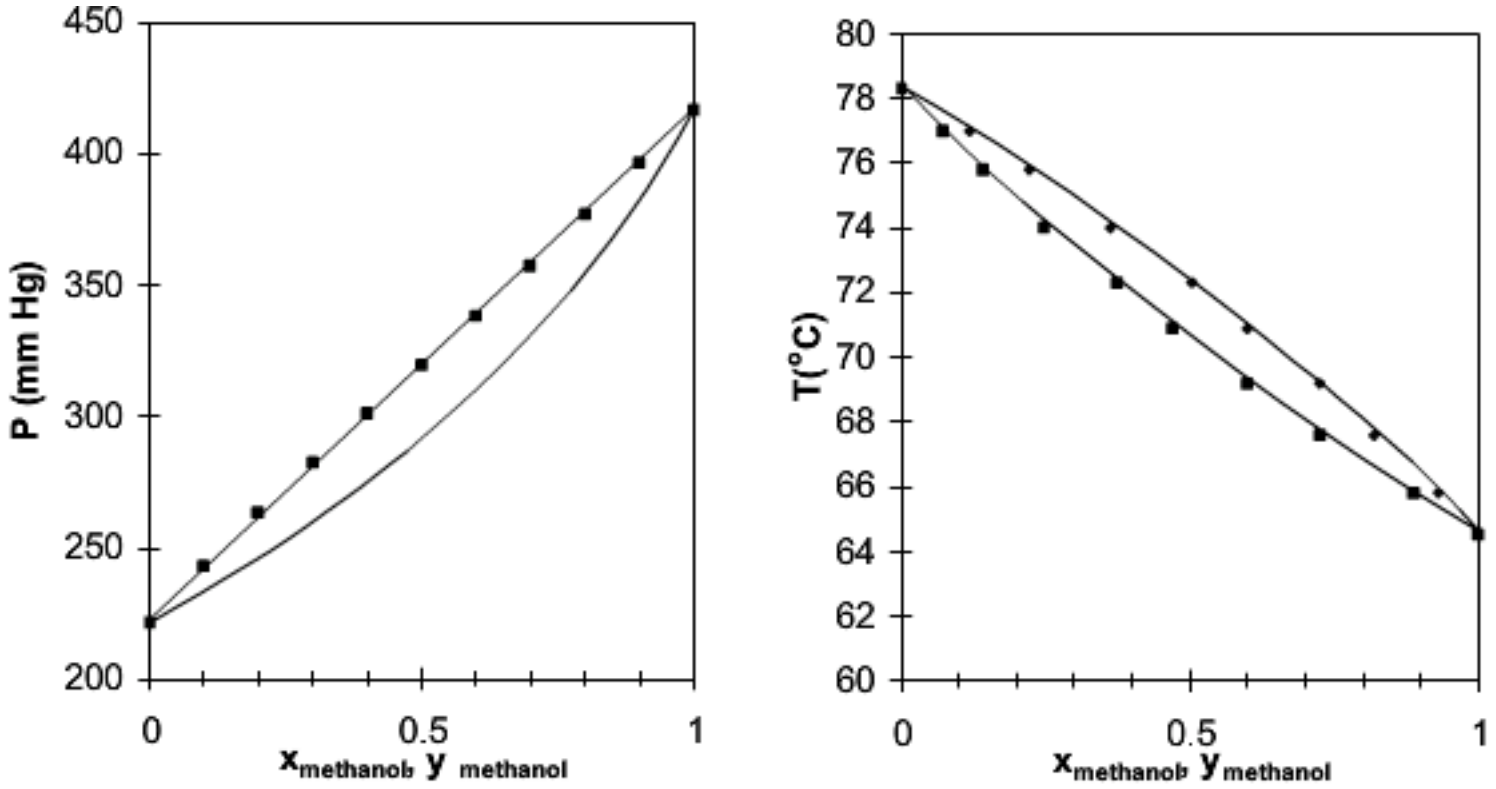


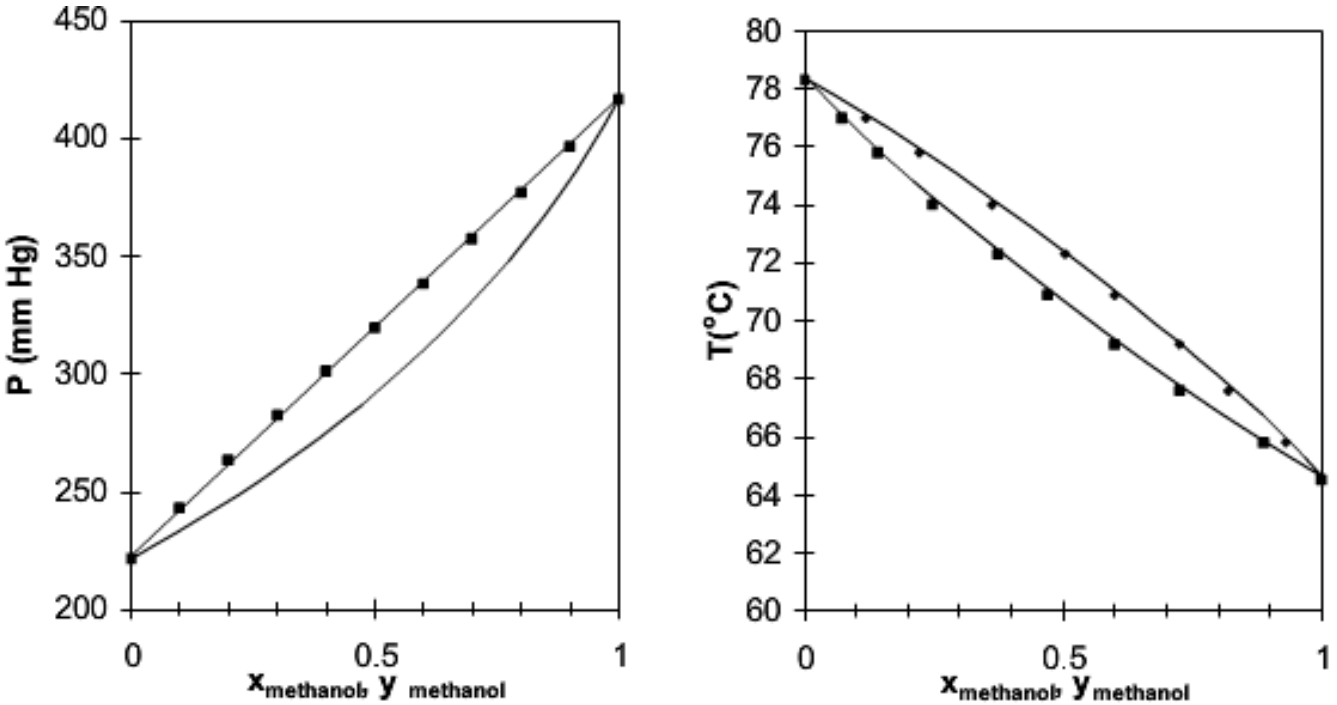
Figure 10.2 *(a), (b). Phase behavior of the methanol-ethanol system. Left figure at 50°C. Right figure at 760 mm Hg. (P-x-y from Schmidt, G.C. 1926. Z. Phys.Chem. 121:221, T-x-y from Wilson, A., Simons, E.L. 1952. Ind. Eng. Chem. 44:2214).*

Raoult's Law for Bubble Pressure.

$$P = P_2^{sat} + x_1(P_1^{sat} - P_2^{sat}) = x_1 P_1^{sat} + (1 - x_1)P_2^{sat} = x_1 P_1^{sat} + x_2 P_2^{sat} \qquad 10.4$$

Dividing by P, we find the form of the bubble objective function summarized in Table 10.1,

$$1 = \frac{P_1^{sat}}{P} x_1 + \frac{P_2^{sat}}{P} x_2 = K_1 x_1 + K_2 x_2 \qquad 10.5$$



(a) (b)

Figure 10.2 *(a), (b). Phase behavior of the methanol-ethanol system. Left figure at 50°C. Right figure at 760 mm Hg. (P-x-y from Schmidt, G.C. 1926. Z. Phys.Chem. 121:221, T-x-y from Wilson, A., Simons, E.L. 1952. Ind. Eng. Chem. 44:2214).*

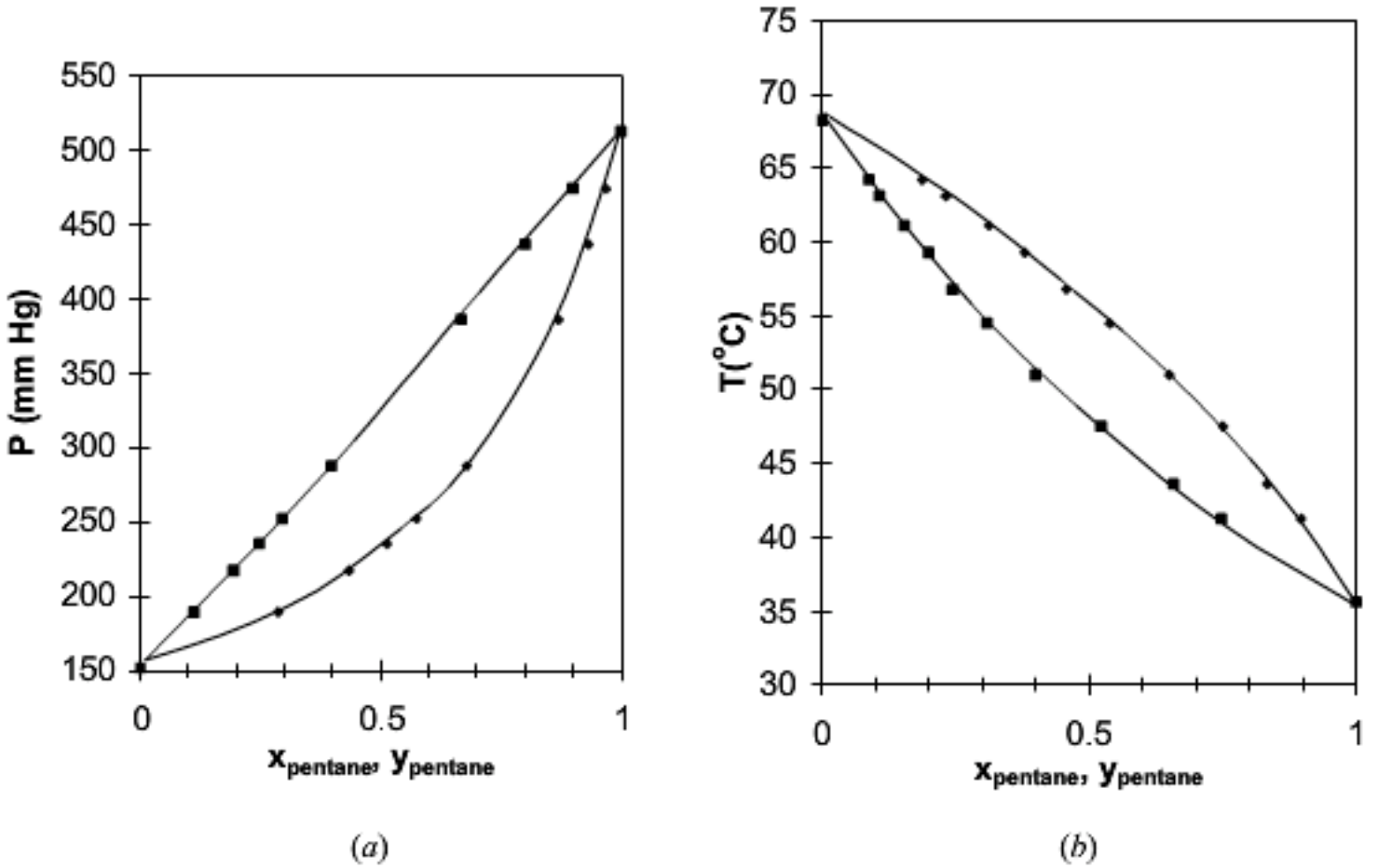


Figure 10.3 *(a), (b) Phase behavior of the pentane-hexane system. Left figure at 25°C. Right figure at 750 mm Hg. (P-x-y from Chen, S.S., Zwolinski, B.J. 1974. J.Chem. Soc. Faraday Trans. 70: 1133, T-x-y from Tenn, F.G., Missen, R.W. 1963. Can. J. Chem. Eng. 41:12).*

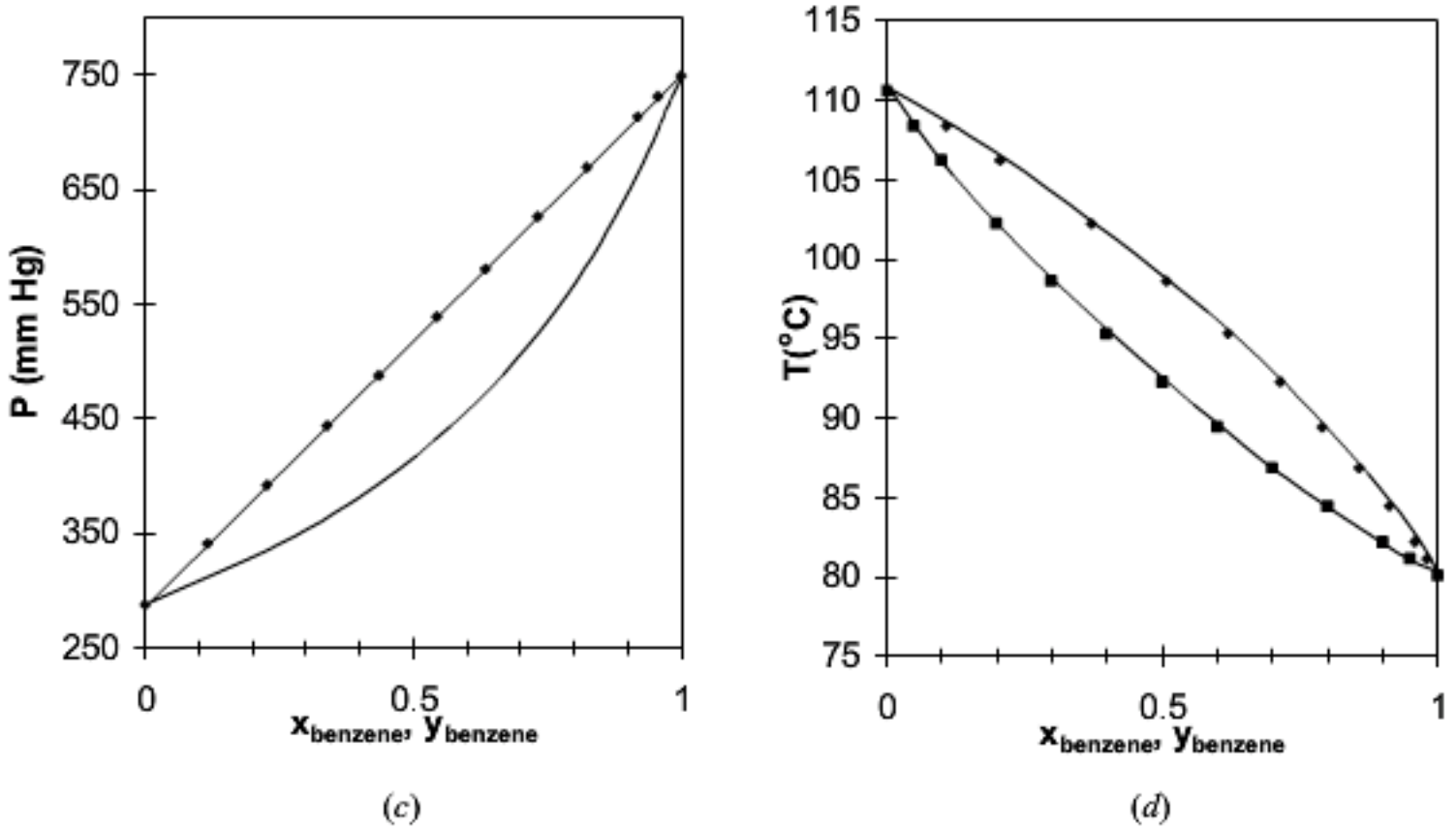


Figure 10.3 *(c); (d) Phase behavior of the benzene-toluene system. Left figure at 79.7°C. Right figure at 760 mm Hg. (P-x-y from Rosanoff, M.A., et al. 1914. J. Am.Chem.Soc. 36:1993, T-x-y from Delzenne, A.O. 1958. Ind. Eng. Chem., Chem. Eng. Data Series. 3:224).*

Therefore, we conclude that the *K*-ratio for Raoult's law[4] is

Raoult's Law
K-ratio.

$$K_i = \frac{P_i^{sat}}{P} \quad \text{or} \quad y_i P = x_i P_i^{sat} \tag{10.6}$$

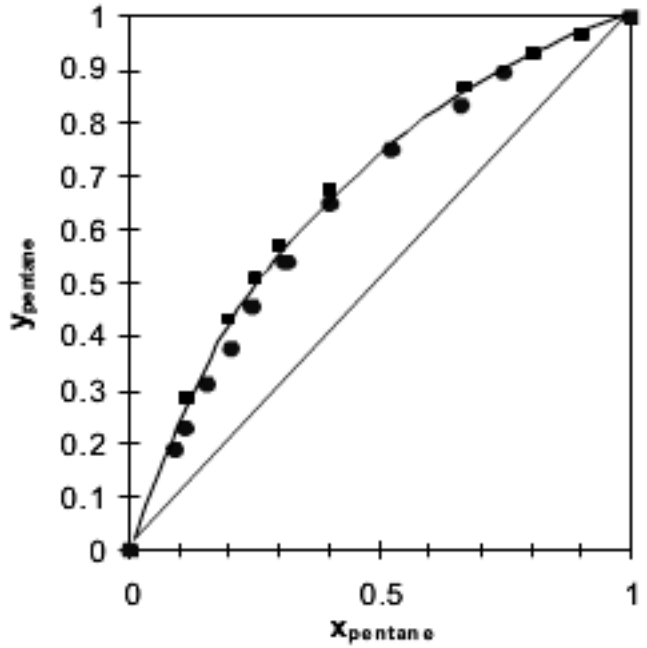


Figure 10.4 *Data from Fig. 10.3 plotted with coexisting liquid and vapor values for each experimental tie line, resulting in the x-y plot. Note that the data do not superimpose exactly because one data set is isobaric and the other set is isothermal. Squares are T-x-y data. Circles are P-x-y data. The diagonal is traditionally drawn in an x-y figure, and the data never cross the diagonal for systems that follow Raoult's law.*

Shortcut Estimation of VLE *K*-ratios

Therefore, we conclude that the *K*-ratio for Raoult's law[4] is

Raoult's Law *K*-ratio.

$$K_i = \frac{P_i^{sat}}{P} \quad \text{or} \quad y_i P = x_i P_i^{sat} \qquad 10.6$$

$$K_i = \frac{P_i^{sat}}{P} \approx \frac{P_{c,i}\,10^{\frac{7}{3}(1+\omega)\left(1-\frac{1}{T_{r,i}}\right)}}{P}$$

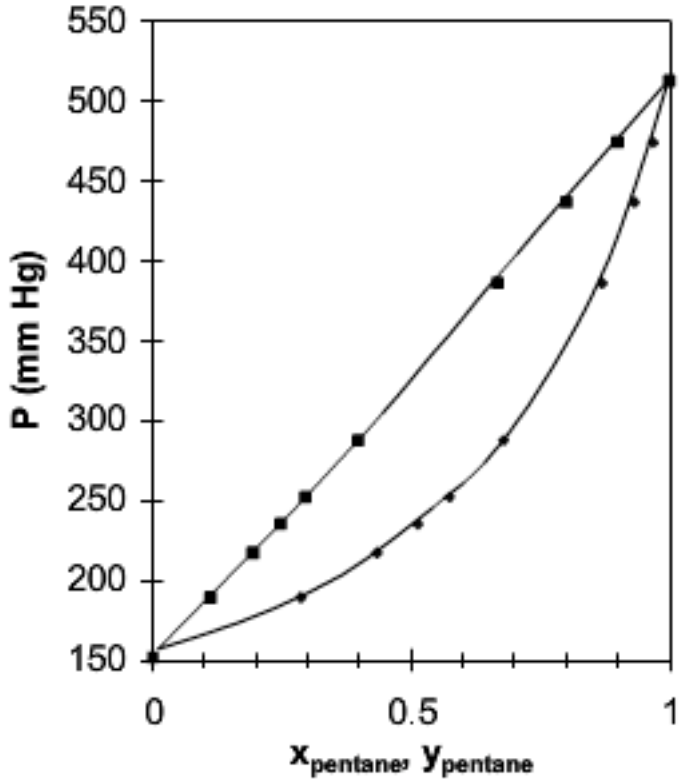
Shortcut *K*-ratio 10.7

Bubble Pressure

For a **bubble-pressure** calculation, writing $\sum_i y_i = 1$ as $\sum_i K_i x_i = 1$, which is $\sum_i \frac{P_i^{sat}}{P} x_i = 1$. Multiplying by P, we may write

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} \qquad 10.8$$

$$y_i = x_i P_i^{sat} / P = K_i x_i \qquad 10.9$$



Dew Pressure

For a **dew-pressure** calculation, writing $\sum_i x_i = 1$ as $\sum_i (y_i/K_i) = 1$ and rearranging:

$$\frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{P_2^{sat}} = 1 \qquad 10.10$$

which may be rearranged and solved without iteration, because the vapor pressures are fixed at the specified temperature:

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} \qquad 10.11$$

Once the dew pressure is calculated, the value can be reinserted into Eqn. 10.6 to find the liquid mole fractions:

$$x_i = y_i P / P_i^{sat} = y_i / K_i \qquad 10.12$$

Bubble Temperature

For a **bubble-temperature** calculation, writing $\sum_i y_i = 1$ as $\sum_i K_i x_i = 1$, and rearranging:

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} \qquad 10.13$$

To solve this equation, it is necessary to iterate on temperature (which changes P_i^{sat}) until P equals the specified pressure. Then the vapor phase mole fractions are calculated using Eqn. 10.9.

$$y_i = x_i P_i^{sat} / P = K_i x_i \qquad 10.9$$

Dew Temperature

For a **dew-temperature** calculation, writing $\sum_i x_i = 1$ as $\sum_i (y_i / K_i) = 1$, and rearranging:

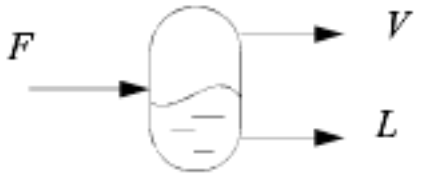
$$P = \frac{1}{\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}} \qquad 10.14$$

To solve this equation, it is necessary to iterate on temperature (which changes P_i^{sat}) until P equals the specified pressure. Then the liquid phase mole fractions are calculated using Eqn. 10.12.

$$x_i = y_i P / P_i^{sat} = y_i / K_i \qquad 10.12$$

General Flash

Figure 10.5 *Illustration of a flash drum and variable definitions for streams. Note that F need not be a liquid; F may be all vapor or partial vapor. The principles can be applied to a nonflowing system as described for a binary on page 371.*



To apply the procedure, the overall composition of the components, z_i, total feed flow rate, F, and outlet T and P just need to be known before the procedure is started.

$$L/F = 1 - V/F$$

$$z_i = x_i(L/F) + y_i(V/F)$$

$$z_i = x_i[(1 - V/F) + K_i(V/F)]$$

$$x_i = \frac{z_i}{1 + (V/F)(K_i - 1)} \qquad 10.15$$

$$y_i = \frac{z_i K_i}{1 + (V/F)(K_i - 1)} \qquad 10.16$$

One obvious thing to do at this point is to iterate to find the *V/F* ratio which satisfies $\sum_i x_i = 1$. But the flash problem is different from the dew- and bubble-point problems because we must also solve $\sum_i y_i = 1$. Fortunately, a reliable successive substitution method has been developed by Rachford and Rice[6] to solve this problem using the objective function $\sum_i x_i - \sum_i y_i = 0$. Introducing the variable $D_i \equiv x_i - y_i$ to denote the difference between x_i and y_i for each component, $\sum_i x_i - \sum_i y_i = \sum_i (x_i - y_i) = \sum_i D_i = 0$, we iterate on *V/F* until the sum approaches zero. For a binary system, using the K_i ratios, the objective function becomes

$$\sum_i x_i - \sum_i y_i = (x_1 - y_1) + (x_2 - y_2) = D_1 + D_2 \qquad 10.17$$

$$= \frac{z_1(1-K_1)}{1+(V/F)(K_i-1)} + \frac{z_2(1-K_2)}{1+(V/F)(K_i-1)} = 0$$

The steady-state energy balance for an general flash is given by

$$\begin{aligned} 0 &= FH^F - LH^L - VH^V + \underline{\underline{\dot{Q}}} \\ &= F\left(\sum_i z_i H_i^F + \Delta H_{mix}^F\right) - L\left(\sum_i x_i H_i^L + \Delta H_{mix}^L\right) - V\left(\sum_i y_i H_i^V + \Delta H_{mix}^V\right) + \underline{\underline{\dot{Q}}} \end{aligned} \qquad 10.18$$

where we indicate a common method of calculation of the enthalpy of a mixture as the sum of the component enthalpies and the heat of mixing (Eqn. 3.24 on page 105). Writing in terms of *V/F:*

$$0 = \left(\sum_i z_i H_i^F + \Delta H_{mix}^F\right) - \left(1 - \frac{V}{F}\right)\left(\sum_i x_i H_i^L + \Delta H_{mix}^L\right) - \frac{V}{F}\left(\sum_i y_i H_i^V + \Delta H_{mix}^V\right) + \frac{\underline{\underline{\dot{Q}}}}{F} \qquad 10.19$$

Adiabatic Flash

An adiabatic flash differs from an isothermal flash because $\dot{Q} = 0$ in Eqn. 10.19. The adiabatic conditions will result in a temperature change from the feed conditions that is often significant. A typical scenario involves an outlet pressure less than the inlet pressure, resulting in an evaporation of a fraction of the feed. Because evaporation is endothermic, this type of flash results in a temperature drop (often significant). We have seen this type of calculation for pure fluids using throttles in Chapter 5. The additional complication with a mixture is that the components will distribute based on their different volatilities. The objective of an adiabatic flash calculation is to determine the outlet temperature in addition to the L and V compositions. An adiabatic flash requires that Eqn. 10.19, ($\dot{Q}$=0), must be solved simultaneously with Eqn. 10.17. The vapor and liquid mole fractions for Eqn. 10.19 are determined from Eqns. 10.15 and 10.16. The method is complex enough that even simple assumptions, such as ideal mixing ($\Delta H_{mix} = 0$), benefit from a computer algorithm.

The algorithm to solve for the adiabatic flash depends on the differences in boiling points of the components. Usually the boiling points are different enough that an initial guess of T is used in VLE Eqn. 10.17 (where V and L are assumed to exit at the same T) to find an initial V/F where $0 < V/F < 1$. With that initial V/F, then the V and L compositions (Eqns. 10.15 and 10.16) and then the energy balance (Eqn. 10.19) are evaluated, often scaling Eqn. 10.19 by dividing by 1000 when the enthalpy values are large. If the energy balance is not satisfied, then a new T trial is inserted into Eqn. 10.17 and the loop continues. Eqn. 10.19 is monotonic in T and increases when T decreases. When the boiling points are very close for all components, such as with isomers, the calculation converges better with an initial guess of V/F in Eqn. 10.17, which is solved by trial and error for the T which satisfies the equation. The L and V compositions and T are then used for the outlet enthalpies in Eqn. 10.19 to generate a new value for V/F and the iteration continues until convergence.

10.4 MULTICOMPONENT VLE RAOULT'S LAW CALCULATIONS

Extending our equations to multicomponent systems is straightforward. For a bubble calculation we have

$$1 = \left(\sum_i x_i P_i^{sat}\right)/P = \sum_i x_i K_i \qquad 10.20$$

For a dew calculation we have

$$1 = P\sum_i \frac{y_i}{P_i^{sat}} = \sum_i \frac{y_i}{K_i} \qquad 10.21$$

These equations may be used for bubble- or dew-pressure calculations without iterations. For bubble- or dew-point temperatures, iteration is required. A first guess may be obtained from one of the following formulas:

$$T_{\text{bubble guess}} = \sum_i x_i T_i^{sat}$$

$$T_{\text{dew guess}} = \frac{\sum_i y_i T_{r,i} T_i^{sat}}{\sum_i y_i T_{c,i}} \quad \text{or} \quad T_{\text{dew guess}} = \sum_i y_i T_i^{sat} \qquad 10.22$$

For flash calculations, the general formula is:

$$\sum_i x_i - \sum_i y_i = \sum_i D_i = \sum_i \frac{z_i(1-K_i)}{1+(V/F)(K_i-1)} = 0 \qquad 10.23$$

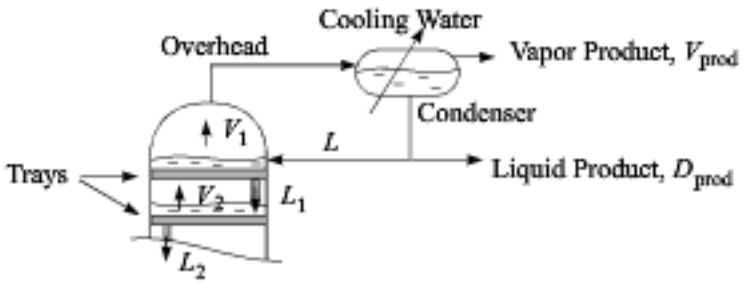
to find L/F and x_i and y_i are then found using Eqns. 10.15 and 10.16.

Example 10.1 Bubble and dew temperatures and isothermal flash of ideal solutions

The overhead from a distillation column is to have the following composition:

	z(Overhead)
Propane	0.23
Isobutane	0.67
n-Butane	0.10
Total	1.00

A schematic of the top of a distillation column is shown below. The overhead stream in relation to the column and condenser is shown where V_{prod} represents vapor flow and D_{prod} represents liquid flow. *In an ideal column, the vapor leaving each tray (going up) is in phase equilibrium with the liquid leaving the same tray (going down).* If the cooling water to the condenser is turned off, then only vapor product will be obtained, but this is not typical because the column works better with some liquid L returning to the column. To obtain liquid product only, cooling water is provided and the vapor product stream is turned off, and the condenser is known as a **total condenser.** If cooling water is provided to partially condense the vapor stream, the liquid product stream is typically turned off. Then the condenser provides additional separation, operating as a **partial condenser.** *In an ideal partial condenser, the exiting vapor and liquid leave in phase equilibrium with each other.*



(a) Using the shortcut K-ratio, calculate the temperature at which the condenser must operate in order to condense the overhead product completely at 8 bar.

(b) Using the shortcut K-ratio, and assuming the overhead product vapors are in equilibrium with the liquid on the top plate of the column, calculate the temperature of the overhead vapors and the composition of the liquid on the top plate when operating at the pressure of part *a*.

(c) The vapors are condensed by a partial condenser operating at 8 bar and 320 K. Using the shortcut K-ratio, what fraction of liquid is condensed?

Example 10.1 Bubble and dew temperatures and isothermal flash of ideal solutions (Continued)

Solution: Use the shortcut estimates of the K-ratios. Use of a solver tool is recommended after developing an understanding of the manual iterations summarized below.

(a) To totally condense the overhead product, the mixture must be at the bubble-point temperature or lower. The maximum temperature is the bubble-point temperature. To find the bubble-point temperature for the ternary system, we apply Eqn. 10.20 extended to three components. The calculation requires trial-and-error iteration on temperature as summarized in Table 10.1.

Tabulated below, the shortcut K-ratio is calculated using Eqn. 10.7 at each temperature guess at 8 bar, and the y values from Eqn. 10.9 are summed to check for convergence following the procedure set forth in Table 10.1. Iterations are repeated until the y's sum to 1.

	Guess $T = 310$ K		Guess $T = 320$ K	
	K_i	y_i	K_i	y_i
C_3	1.61	0.370	2.03	0.466
iC_4	0.616	0.413	0.80	0.536
nC_4	0.438	0.044	0.58	0.058
	$\Sigma y_i =$	0.827	$\Sigma y_i =$	1.061

The temperature has been bracketed, interpolating,

$$T = 325 + \left(\frac{1.00 - 0.994}{1.123 - 0.994}\right)(320 - 325) = 324.8 \text{ K} \qquad 10.24$$

The temperature has been bracketed, interpolating,

$$\Rightarrow T = 310 + \left(\frac{1.000 - 0.827}{1.061 - 0.827}\right)(320 - 310) = 317 \text{ K}$$

(b) The saturated vapor leaving the tray is in equilibrium with the liquid and is at its dew-point temperature at 8 bar. Eqn. 10.21 is used. The calculation requires iteration on temperature. Calculating the K_i ratios as in part (a), the liquid phase compositions are calculated at each iteration using Eqn. 10.12 until the values sum to 1.

	Guess $T = 325$ K		Guess $T = 320$ K	
	K_i	x_i	K_i	x_i
C_3	2.26	0.102	2.03	0.113
iC_4	0.905	0.740	0.80	0.838
nC_4	0.658	0.152	0.58	0.172
	$\Sigma x_i =$	0.994	$\Sigma x_i =$	1.123

It is easy to create an Excel spreadsheet to do these calculations quickly (e.g., Flshr.xlsx can be modified).

Example 10.1 Bubble and dew temperatures and isothermal flash of ideal solutions (Continued)

Repeating the procedure at this temperature a final time results in the liquid compositions,

	Guess	$T = 324.8$ K
	K_i	x_i
C_3	2.25	0.102
iC_4	0.900	0.744
nC_4	0.654	0.153
	$\Sigma x_i =$	0.999

(c) Recognize that the solution involves an isothermal flash calculation because P and T are both specified. Begin by noting that the specified condenser temperature is between the bubble temperature, 317 K, and the dew temperature, 324 K, so vapor-liquid equilibrium is indeed possible. Because T and P are already set, Eqn. 10.7 is used to calculate the K-ratio for each component. Then, we seek a solution for Eqn 10.23 at 320 K and 8 bar. In the general flash routine, F_{flash}, V_{flash}, and L_{flash} are used to denote the flow rates for the flash drum and we must adapt the flash variables to the column stream names. We add "flash" and "column" subscript descriptors for increased clarity. In the solution, F_{flash}, V_{flash}, and L_{flash} represent the flow rates for the partial condenser, $F_{flash} = V_{1,column}$, $V_{flash} = V_{prod}$, and $L_{flash} = D_{prod} + L_{column}$. In the summarized calculations below, $V_{flash}/F_{flash} = V_{prod}/V_{1,column}$ and D_i in the table is the objective variable for the flash calculation as used in Eqn. 10.23, not the column liquid product flow rate D_{prod}. Each table column summarizes a guess for flash ratio V_{flash}/F_{flash} and the resultant flash objective variable D_i. The composition of the feed is given by z_i as conventional for a flash calculation, which is the composition of $V_{1,column}$.

Flshr.xlsx or Chap10/Flshr.m can be modified to work this example.

A summary of the isothermal flash calculation is given below.:

	F_{flash}		Guess $V_{flash}/F_{flash} = 0.5$	Guess $V_{flash}/F_{flash} = 0.4$	Guess $V_{flash}/F_{flash} = 0.23$
	z_i	K_i	$D_i = x_i - y_i$	D_i	D_i
C_3	0.23	2.03	−0.1564	−0.1678	−0.1915
iC_4	0.67	0.80	0.1489	0.1457	0.1405
nC_4	0.10	0.58	0.0532	0.0505	0.0465
			sum = 0.0457	sum = 0.0284	sum = −0.0045

Example 10.1 Bubble and dew temperatures and isothermal flash of ideal solutions (Continued)

Interpolating between the last two results that bracket the answer,

$$\frac{V_{\text{flash}}}{F_{\text{flash}}} = 0.23 + \left(\frac{0.4 - 0.23}{0.0284 + 0.0045}\right)(0. + 0.0045) = 0.2533$$

$V_{\text{flash}}/F_{\text{flash}} = 0.25$, applying Eqns. 10.15 and 10.16,

$\Rightarrow \{x_i\} = \{0.1829, 0.7053, 0.1117\}$ and $\{y_i\} = \{0.3713, 0.5642, 0.0648\}$

The compositions can be confirmed to be converged. The outlet composition of the vapor, V_{prod}, is given by $\{y_i\}$ and it is clearly more enriched in the volatile components than the inlet from the top of the column $V_{1,\text{column}}$.

Note: *The flash problem converges more slowly than the bubble- and dew-point calculations, so the third iteration is necessary.*

Example 10.2 Adiabatic flash

Ethanol + methanol form a nearly ideal solution as shown in Fig. 10.2. An equimolar feed at 760 mmHg is subjected to an adiabatic flash operating at 200 mmHg. Feed enters at 70°C and 43 mol/min. Find the exiting stream temperatures, flow rates, and compositions. Assume ideal solutions and use the Antoine equation for vapor pressures.

Chap10/ Ex10_02.m.

Solution: This is a direct application of a procedure, so it is clear which VLE routine to use: the FA row of Table 10.1. We must combine the VLE procedure with energy balance. A bubble-pressure calculation at 70°C (not shown) shows that the feed is all liquid. Two solutions are provided using different pathways for the enthalpy calculations. Both solutions will use the same flash calculation procedures and the Antoine equation is used with {methanol, ethanol}:

A = {8.081, 8.1122}, B = {1582.3, 1592.9}, C = {239.73, 226.18}

Solution 1. This solution method calculates component enthalpies using a reference state of liquid at 25°C for all species where we set $H_R = 0$. The enthalpy calculations use the pathway of Fig. 2.6(a). The pathway is taken through the boiling point of each component, as in Example 3.3. To compute stream enthalpies, we use ideal solutions as shown in Example 3.3, ignoring heat of mixing. Heat capacity constants and heats of vaporization are taken from Appendix E.

The solution requires a guess of T resulting in $0 \le V/F \le 1$ that provides two phases, and then a check of the energy balance. Due to the complexity of the calculation, we iterate on the T guess manually, and automate the tedious parts of solving for V/F and checking the energy balance. The solution is provided in MATLAB file Ex10_02.m. Some intermediate results are tabulated.

Because a computer is used, we skip preliminary bubble and dew calculations. Note that we do not tabulate all values until $0 \le V/F \le 1$. The first guess of 45°C is above the dew temperature. The second guess of 35°C is below the bubble temperature. The next guess happens to give a condition close to the bubble temperature, so we raise the temperature guess slightly. The column *OBJEB* = (Eqn. 10.19)/1000. The compositions and enthalpies are shown below and the last row is converged. The exiting flow rates are $V = V/F(43) = 0.09(43) = 3.87$ mol/min, and $L = 43 - 3.87 = 39.13$ mol/min. About 9% (molar basis) of the inlet is flashed, and the outlet temperature is 40.2°C compared to an inlet of 70°C.

$T^{out}(C)$	V/F	OBJEB	x_{EtOH}	y_{EtOH}	H^F(J/mol)	H^L(J/mol)	H^V(J/mol)
45	2.98						
35	–9.32						
40	0.001	3.137	0.50	0.33	4672	1481	39,149
41	0.43	–13.30	0.57	0.40	4672	1618	39,539
40.2	0.09	–0.22	0.515	0.349	4672	1508	39,225

Solution 2. This solution method calculates component enthalpies using the pathway of Fig. 2.6(c), the reference state of the elements at 25°C, the heats of formation of ideal gases, the generalized correlation for heat of vaporization in Eqn. 2.45, and the Cp^{ig}(25°C) from the back flap. The results are slightly different from Solution 1, owing to the imprecision of Eqn. 2.45 and differences between the heat capacities. Process simulation software typically uses this enthalpy path and reference state.

We begin by finding the enthalpy of the feed relative to the elements at 25°C, noting that it is a liquid ideal solution. $H^F = H^L(70°C) = \Sigma\, x_i(\Delta H^\circ_{f,i} + Cp^{ig}(T - T_R) - \Delta H_i^{vap}) = 0.5(-200{,}940 + 5.28(8.314)(70 - 25) - 35{,}976) + 0.5(-234{,}950 + 7.88(8.314)(70 - 25) - 38{,}595) = -252{,}769$ J/mol. This takes care of the first term in Eqn. 10.19. Noting that the feed is liquid, we might suspect the flash outlet to be mostly liquid. Performing a bubble-temperature calculation at 200 mmHg gives $T = 40.00$°C and $H^L(40°C) = -256{,}901$ and with no vapor stream results in $Q = -4132$ J/mol.[a] The temperature must be slightly higher to move Q toward zero. Suppose we "guessed" that the temperature is 40.23°C.[b] Then the flash calculation gives $x_{EtOH} = 0.5173$, $y_{EtOH} = 0.3515$, $V/F = 0.1042$, $H^L(40.23°C) = -257{,}502$. The formula for H^V is similar to that for H^L but omits the ΔH_i^{vap} contribution and replaces x_i with y_i, so $H^V(40.23°C) = -212{,}088$. Following Eqn. 10.19, $Q = (1 - 0.1042)(-257{,}502) + 0.1042(-212{,}088) + 252{,}769 = 0.1$ J/mol. We may assume that 0.1 J/mol is sufficiently close to zero.

volatile organic compounds (VOCs),

(also known as the **head space**). In some cases, the inert head space gas flows through the vessel, and is called a **purge** or **sweep** gas. These gases typically have negligible solubilities in the liquid phase and are thus considered **noncondensable.** There are several common types of unit operations encountered with VOC emissions, which will be covered individually.

Filling or Charging

During filling of a tank with a volatile component, gas is displaced from the head space. The displaced gas is assumed to be saturated with the volatile components as predicted with Raoult's law and the ideal gas law. Initially in the head space, $n^i_{head} = (P\underline{V}^i_{head})/(RT)$ and after filling, $n^f_{head} = (P\underline{V}^f_{head})/(RT)$, where the subscript *head* indicates the head space. The volume of liquid charged is equal to the volume change of the head space. The mole fractions of the VOC components are determined by Raoult's law, and the noncondensable gas makes up the balance of the head space. The moles of VOC emission from the tank are estimated by $y_i(n^i_{head} - n^f_{head})$ for each VOC.

Purge Gas (Liquid VOC Present)

When a purge (sweep) gas flows through a vessel containing a liquid VOC, the effluent will contain VOC emissions. At the upper limit, the vessel effluent is assumed to be saturated with VOC as predicted by Raoult's law. For VOC component *i*,

$$\Delta n_i = n_{sweep} \cdot k_m (y_i / y_{nc}) \qquad 10.25$$

where $y_{nc} = 1 - \sum_i y_i$, where the sum is over VOCs only. The variable k_m is the saturation level, and is set to 1 for the assumption of saturation and adjusted lower if justified when the purge gas is known to be unsaturated. The flow of noncondensables n_{sweep} can be related to a volumetric flow of purge gas using the ideal gas law,

$$n_{sweep} = \dot{n}t = \frac{P\dot{V}_{sweep}}{RT} t \qquad 10.26$$

Purge Gas (No Liquid VOC Present)

Vessels need to be purged for changeover of reactants or before performing maintenance. After draining all liquid, VOC vapors remain in the vessel at the saturation level present before draining.

The typical assumption upon purging is that the vessel is well mixed. A mole balance on the VOC gives $dn_i/dt = -y_i \dot{n}_{sweep}$; dividing by y_i the equation becomes $dn_i/y_i dt = -\dot{n}_{sweep}$. The left-hand side can subsequently be written $n_{tank} dy_i/y_i dt = (P\underline{V}_{tank})/(RT_{tank}) \cdot (dy_i)/(y_i dt)$, and the right-hand side can be written $(P\dot{\underline{V}}_{sweep})/(RT_{sweep})$. When the sweep gas and tank are at the same temperature, which is usually a valid case, the equation rearranges to $(dy_i)/y_i = (-\dot{\underline{V}}_{sweep}/\underline{V}_{tank})dt$, which integrates to

$$y_i^f = y_i^i \exp\left(\frac{-\dot{\underline{V}}_{sweep}}{\underline{V}_{tank}} t\right) \qquad 10.27$$

The emissions are calculated by

$$\Delta n_i = n_{tank}(y_i^i - y_i^f) \qquad 10.28$$

Heating

During a heating process, emissions arise because the vapors in the head space must expand as the temperature rises. Since vapor pressure increases rapidly with increasing temperature, VOC concentrations in the vapor phase increase also. Detailed calculations of emissions during heating are somewhat tedious, so an approximation is made; the emission of each VOC is based on the arithmetic average of the molar ratio of VOC to noncondensable gas at the beginning and the end of the heating multiplied by the total moles of noncondensable gas leaving the vessel. At the beginning of the heating, representing the VOC with subscript i and the noncondensables with subscript nc, the ratio of interest is $(n_i/n_{nc})^i = (y_i/y_{nc})^i = (y_iP/y_{nc}P)^i$, and at the end $(n_i/n_{nc})^f = (y_i/y_{nc})^f = (y_iP/y_{nc}P)^f$. The emission of VOC component i is calculated as

$$\Delta n_i = \frac{\Delta n_{nc}}{2}\left[\left(\frac{y_i}{y_{nc}}\right)^i + \left(\frac{y_i}{y_{nc}}\right)^f\right] \qquad 10.29$$

where $y_{nc} = 1 - \sum_i y_i$, and the sum is over VOCs only. The value of Δn_{nc} is given by

$$\Delta n_{nc} = \frac{V_{head}}{R}\left[\left(\frac{\left(1-\sum_i y_i\right)P}{T}\right)^i - \left(\frac{\left(1-\sum_i y_i\right)P}{T}\right)^f\right] + \Delta n_{sweep} \qquad 10.30$$

where the summations are over VOCs only and Δn_{sweep} is the total moles of noncondensable that are swept (purged) through the vessel during heating and is set to zero when purging is not used. Eqns. 10.29 and 10.30 can overestimate the emissions substantially if the tank approaches the bubble point of the liquid because y_{nc} approaches zero, and then calculations are more accurately handled by a more tedious integration. The integration can be approximated by using the method presented here over small temperature steps and summing the results.

Depressurization

Three assumptions are made to model depressurizations: The pressure is decreased linearly over time; air leakage into the vessel is negligible; and the process is isothermal. The relationship is then the same as Eqn. 10.29, where Δn_{nc} is calculated by Eqn. 10.30 using $\Delta n_{sweep} = 0$.

$$\Delta n_{nc} = \frac{V_{head}}{R}\left[\left(\frac{\left(1-\sum_i y_i\right)P}{T}\right)^i - \left(\frac{\left(1-\sum_i y_i\right)P}{T}\right)^f\right] + \Delta n_{sweep} \qquad 10.30$$

Flash Point

The **flash point** is a property much different from that represented by the general flash or adiabatic flash discussed earlier. Fire requires fuel, an oxidizer (air in this case), and an ignition source. The flash point is the temperature above which a vapor mixture supports combustion when an ignition source is present. When liquids burn, fire occurs on a liquid surface; the vapors near the surface are burning, not the liquid itself. The flash point is important because it is the temperature at which the **Lower Flammability Limit (LFL)** concentration is reached at the liquid surface. A flash can also occur entirely in the vapor phase. When burning buildings explode in action movies, the movies are depicting the real condition of the vapors in the building reaching the flash point as plastics and other materials decompose. Fire fighters are very cautious entering buildings where a potential for such explosions exist.

$$\sum_i \frac{y_i}{(LFL_i/100)} = 1 \qquad \text{flash point temperature condition for mixture} \qquad 10.31$$

Because combustion requires an oxidizer, each fuel also has an **Upper Flammability Limit (UFL)** above which there is not enough oxygen present to maintain combustion. Most accidents occur near the LFL, which is the motivation for more discussion of LFL. Both the LFL and the UFL are affected by inerts because of the effect on the ratio of oxidizer to fuel.

10.6 RELATING VLE TO DISTILLATION

We introduced some major points about the importance of distillation in Section 3.2. Roughly 80% of separations are done involving distillation and 70% of the capital cost of a chemical plant goes into distillation equipment, and thus the proper application of vapor-liquid equilibria and design are essential. Usually, one distillation column is required to separate any two components. To separate three components to high purity requires two columns. Obtaining four components to high purity requires three columns, and so forth. So a single reactor that requires two reactants and produces two products ($A + B \rightarrow C + D$) would probably require three distillation columns downstream if all the components are desired in high purity. Pharmaceutical and speciality chemical plants have more by-products than bulk chemical plants. This means that chemical engineers need to be fairly familiar with VLE, especially in the fine chemicals industry.

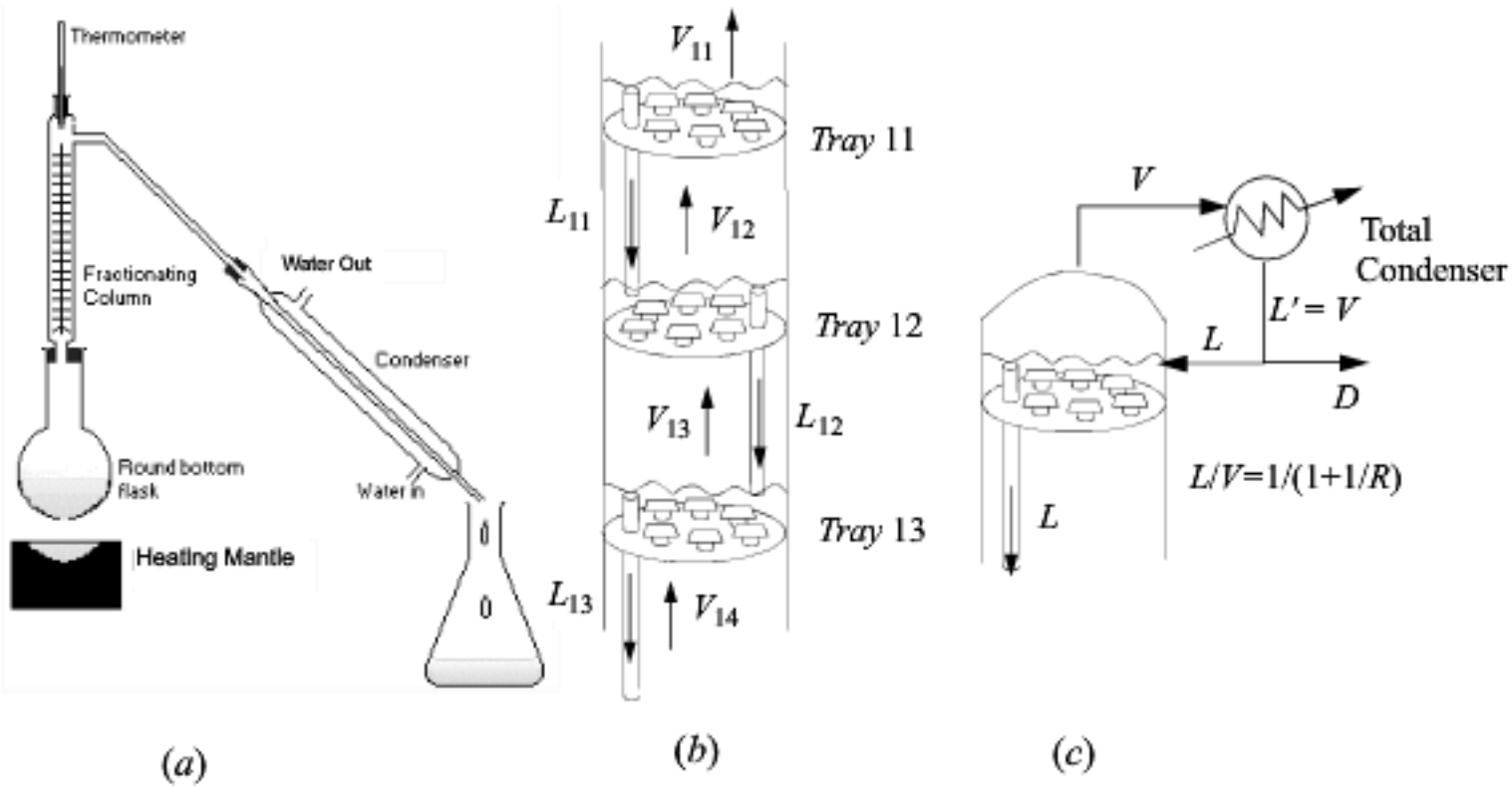


Figure 10.6 *Schematic diagrams of distillation columns. (a) A typical chemistry laboratory distillation apparatus; (b) close-up view of sieve trays showing the holes in the trays, downcomers, and liquid on each tray; (c) a partial condenser operates like a flash unit.*

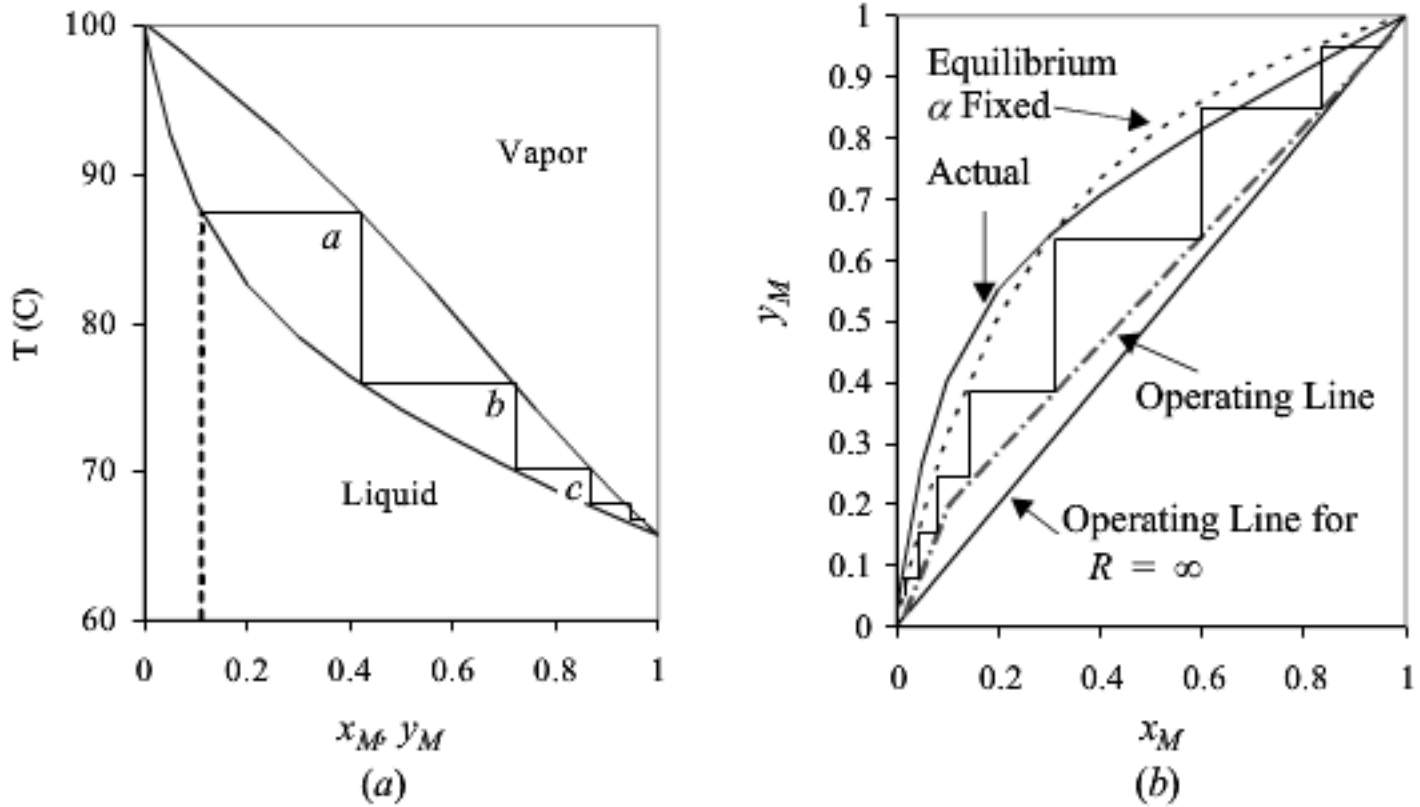
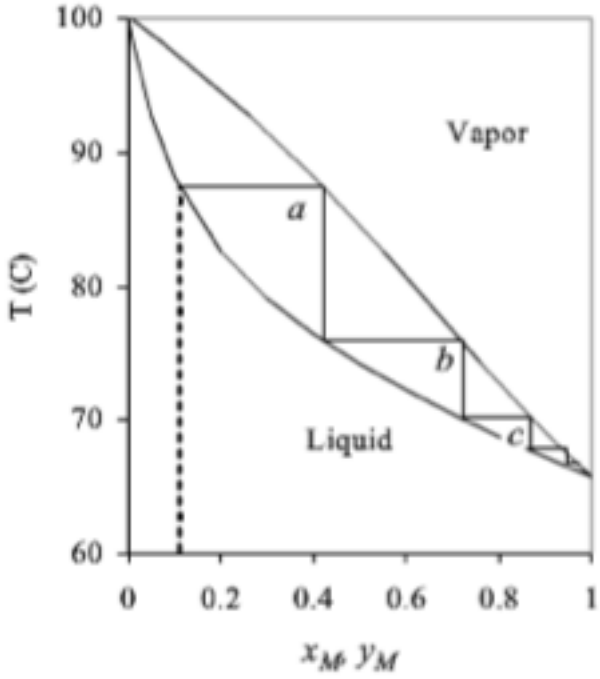
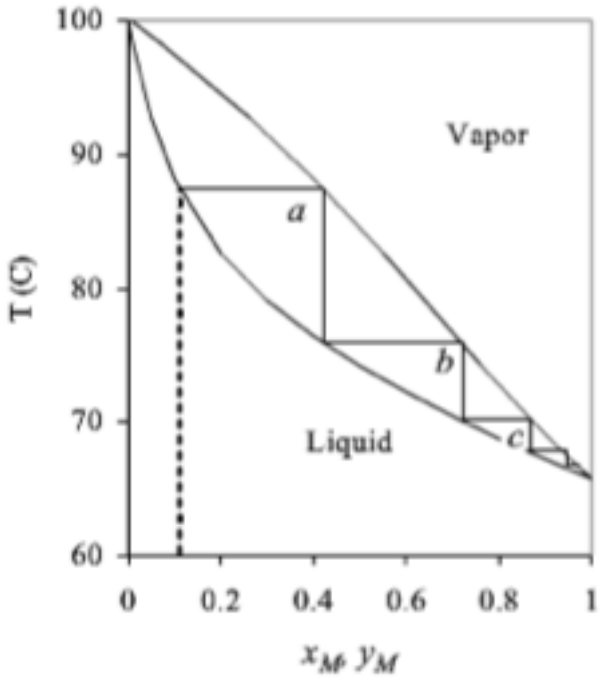


Figure 10.7 *Stage-wise separation of methanol (M) and water. (a) T-x,y diagram at 1 bar, showing stages. (b) McCabe-Thiele analysis based on assuming constant relative volatility,* $\alpha_{LH} = [(\alpha_{LH}^{T})(\alpha_{LH}^{B})]^{1/2}$ *(dotted line) compared with experimental curve.*

The thermodynamics of the methanol + water system are summarized in Fig. 10.7. Fig. 10.7(a) shows that the solution bubble-point temperature is ~87°C. As it boils, the temperature remains constant, but the vapor composition leaving the vessel is ~40 mol% MeOH. Let us call this separation stage *a*. Forty percent is a big improvement over the initial 10%, but it is still mostly water. What can you do to make it more pure? Why not condense the vapor to a liquid and collect it in a separate pot to reboil it? After you have enough solution in that pot, take it to another boiler and perform stage *b*, then repeat for stages *c, d, e* as shown in Fig. 10.7(a). After ~5 stages, you could obtain 98% pure methanol. This is a simplification of multistage distillation at the conceptual level. (Note that most process simulation software numbers stages from the column top which is why we designated stages as letters rather than numbering from the bottom.) As outlined so far, it is inefficient and oversimplified because we considered the liquid phase composition to be invariant while the volatile component was boiling off. Separation textbooks provide the details on the mass balances.



The first law of thermodynamics tells us that energy is conserved. What if we could use the heat of condensing the vapor from stage *a* as the heat of boiling in stage *b*? That would be a big improvement. Furthermore, we can achieve this in minimal space if we use some clever plumbing. If we put the pot for stage *b* on top of stage *a,* and put little holes in the bottom of the pot, then the vapor boils through the holes faster than the liquid can weep back (Fig. 10.6(b)). The boiling point of the mixture on stage *b* is lower than the vapor temperature coming from below (*cf.* Fig. 10.7(a)). When the warmer vapor from stage *a* contacts the cooler liquid on stage *b,* it condenses. But the first law tells us that the heat of condensation must go somewhere. Where? It goes into boiling the liquid on stage *b*. Then we can do the same thing for stages *c, d, e*. This approach is called a tray distillation column and it is very common throughout the chemical industry. Roughly 70% of distillation columns are tray type.



Most mixtures contain more than two components. It is common, however, to design the multi-component column based on the separation of two key components. Because boiling point (in the absence of azeotropes discussed later) increases with M_w, it is common to discuss separation based on *light* components (more volatile) moving up the column, and *heavy* components moving down. For preliminary column design a volatile **light key** (typically low M_w, thus *light*) and less volatile **heavy key** component are designated. Splitting two key components implicitly splits components lighter than the "light key" component from components heavier than the "heavy key" component. The **split** (S) is the fraction that exits with distillate. The light key (LK) component is the least volatile component with a split $S_{LK} > 0.5$. System components lighter than the light key must be even more volatile and exit as distillate. For example, consider a distillation of hexane, octane, decane, and dodecane. If we designate octane as the light key, then the of hexane should also go out the top. The heavy key is the lightest component (most volatile) with a split $S_{HK} < 0.5$. In the example, we could select decane as the heavy key and thus dodecane would go out the bottom also. In a perfect world, the splits would be 100% for the light key and 0% for the heavy key, but that would require an infinitely tall distillation column. More typical splits are 99% and 1%.

Light key and heavy key components are used in preliminary column design.

The split fractions define the relevant mass balances in distillation. The thermodynamics relevant to distillation is implemented using the **relative volatility** in terms of the VLE K-ratios,

Relative volatility.

$$\alpha_{ij} = K_i/K_j \tag{10.32}$$

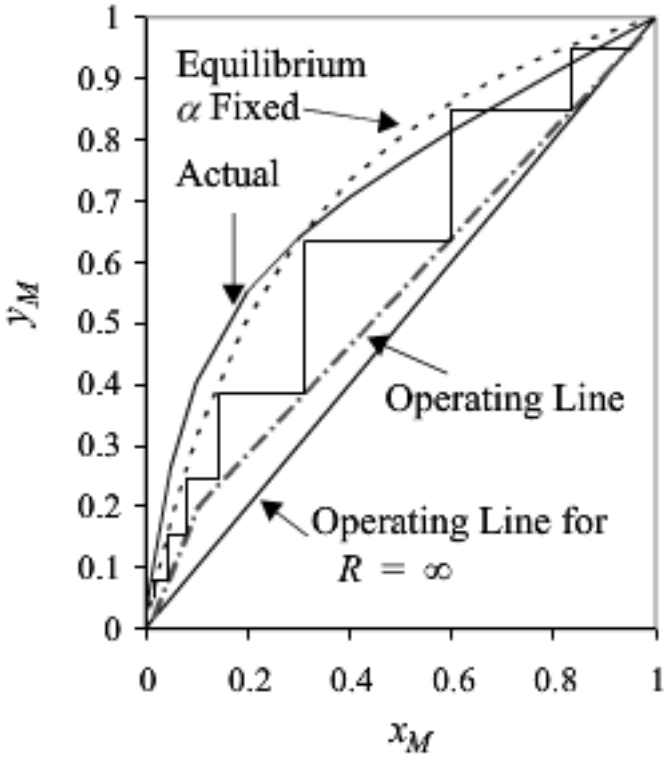
For the case of light and heavy key components,

$$\alpha_{LH} = K_{LK}/K_{HK} \tag{10.33}$$

For Raoult's law, the K-ratios are independent of composition, and thus is the relative volatility,

$$\alpha_{ij} = K_i/K_j = (P_i^{sat}/P)/(P_j^{sat}/P) = P_i^{sat}/P_j^{sat} \qquad \text{Raoult's law} \tag{10.34}$$

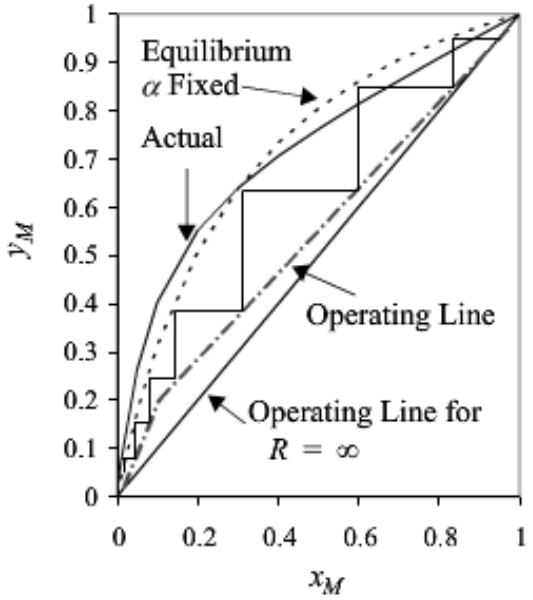
For systems that don't follow Raoult's law, the relative volatility may vary through the column owing to composition changes, but distillation is feasible as long as $\alpha_{LH} > 1$. (We will show the analysis for the nonideal α_{ij} calculation in Section 11.11 on page 442.) The presence of other components is of secondary concern for preliminary column design as long as $\alpha_{LH} > 1$, so shortcut column analysis treats LK and HK as if the mixture were binary. It may be possible to improve α_{LH} through the addition of other components (e.g., extractive distillation), but that merely reinforces the requirement of the overall system to the mandate that $\alpha_{LH} > 1$.



(b) McCabe-Thiele analysis based on assuming constant relative volatility, $\alpha_{LH} = [(\alpha_{LH}^{T})(\alpha_{LH}^{B})]^{1/2}$ *(dotted line) compared with experimental curve.*

$$\alpha_{ij} = K_i/K_j = (P_i^{sat}/P)/(P_j^{sat}/P) = P_i^{sat}/P_j^{sat} \qquad \text{Raoult's law}$$

For the sake of modeling, the tray column is simplest to introduce as illustrated in Fig. 10.7(b). Fig. 10.7(b) focuses on the composition changes only, neglecting the temperature effects. Fig. 10.7(b) also shows the result of approximating that the relative volatility is constant. A larger α_{ij} results in a larger area under the *x*-*y* curve and an easier separation. If $\alpha_{ij} = 1$, the curve collapses on the 45° diagonal. The diagram shows "steps" between the equilibrium line and the operating line. The equilibrium line represents the compositions at each tray as they leave. The operating line represents the compositions between trays. Moving up and down the column, the material balances are shown graphically by stepping back and forth as we relate the material balance "on stage" and "in-between stage." Comparing the curves for actual and constant α_{ij}, note that a similar number of stages is obtained. For the purposes of our model, constant relative volatility is a convenient approximation for the equilibrium curve as shown. But there is still a significant detail that has been omitted in our conceptual outline of distillation. Where did the liquid come from that is on the trays of the tray column?



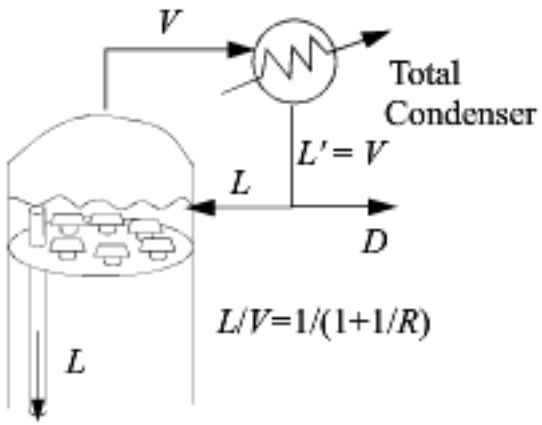


Fig. 10.6(c) shows how the condenser on top of the column pours liquid back down to keep some on the trays. The part that we pour back down the column (L) is called **reflux.** The part that we recover as product is called distillate (D). The ratio of L/D is called the **reflux ratio** (R). The reflux ratio controls the amount of product recovered as distillate. If we actually want to recover some product (i.e., $D \neq 0$), then we must accept some value $R \neq \infty$. Finite values for R lead to the dashed-dot operating lines in Fig. 10.7(b). To understand this, consider that the 45° diagonal on Fig. 10.7(b) corresponds to $L/V = 1$. It turns out that taking distillate from the top of the column leads to slightly less separation on every stage, giving the dashed-dot lines of Fig. 10.7(b). Typical courses in mass transfer operations explain how to estimate the dashed-dot lines from values of R. The key point for now is that the value of R cannot be zero, or we will have no liquid on the trays, and it cannot be infinite or we will recover no product. We can go a little further and say that it must be closer to infinity for a distillation that has a relative volatility very near to unity, because the y-x curve in that case stays very close to the diagonal. Beyond that, we simply need to accept that somebody has analyzed this before and developed some equations for computing the minimum number of stages to achieve a desired separation (at infinite reflux), the minimum reflux ratio, and the actual number of stages. This is indeed the case, and the model equations are presented below.

A shortcut distillation calculation for the height of the column for constant relative volatility can be estimated from the Fenske equation,

$$N_{min} = \frac{\ln\left[\frac{S_{LK}(1-S_{HK})}{S_{HK}(1-S_{LK})}\right]}{\ln \alpha_{LH}^{m}} \quad \text{ideal solutions} \qquad 10.35$$

where N_{min} is the minimum number of theoretical trays at infinite reflux and α_{LH}^{m} is the geometric mean of the relative volatility calculated using the column top and bottom compositions, T and P. Typically, the number of actual trays is $N_{act} \sim 4N_{min}$, with the space between trays being 0.6m. So a column with 99 and 1% splits and a relative volatility of 3 would have $N_{min} = 8.4$ and a height of 20 m. With this background, the importance of the K-ratios and α_{LH} becomes clear. Note that if $\alpha_{LH} = 1$, then $N_{min} = \infty$. The relative volatility changes with composition for nonideal systems, and goes to 1 when an azeotrope exists. Then Eqn. 10.35 is not valid. We discuss such behavior in the

10.7 NONIDEAL SYSTEMS

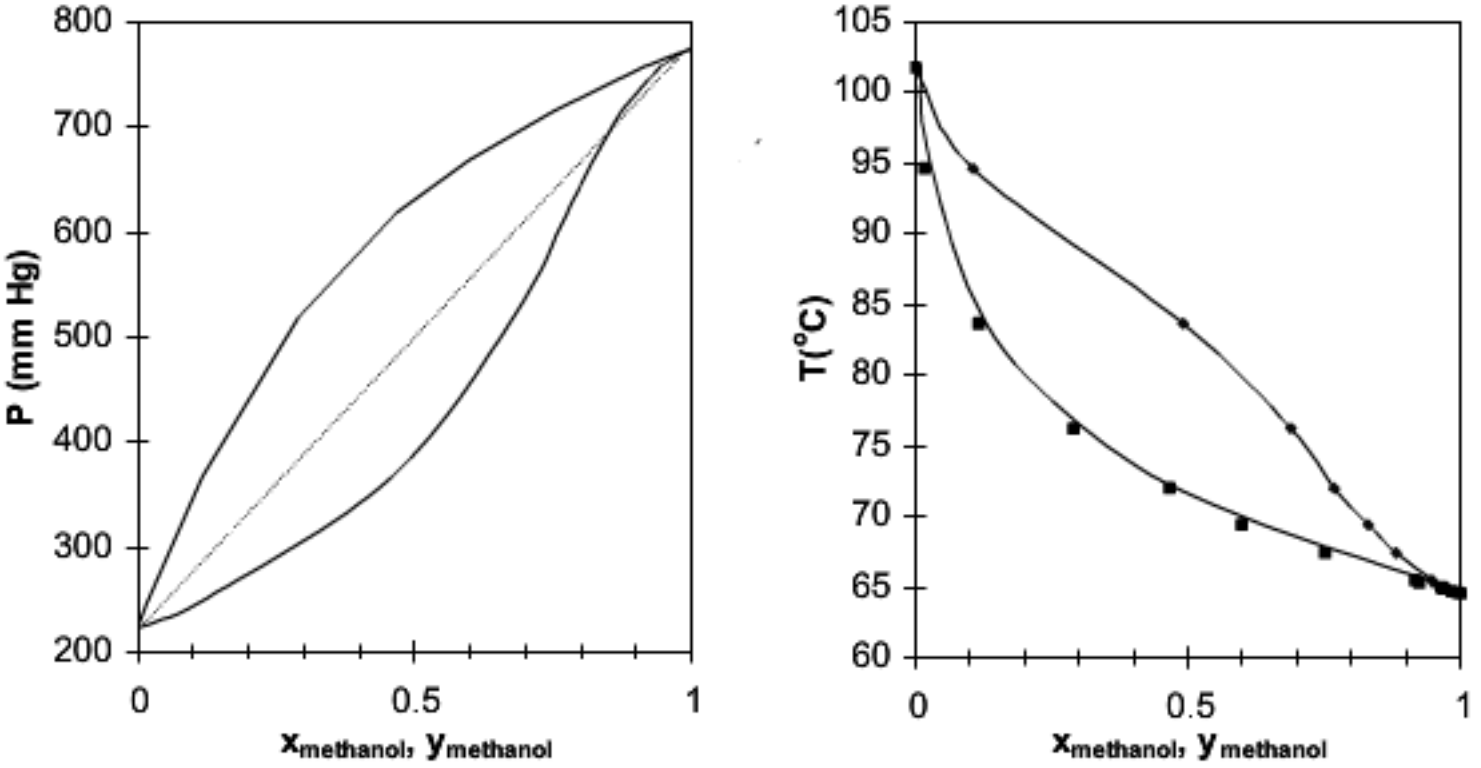


Figure 10.8 *(a), (b) Phase behavior of the methanol + 3-pentanone system. Left figure at 65°C. Right figure at 760 mm Hg. (T-x-y from Glukhareva, M.I., et al. 1976. Zh. Prikl. Khim. (Leningrad) 49:660, P-x-y calculated from fit of T-x-y.)*

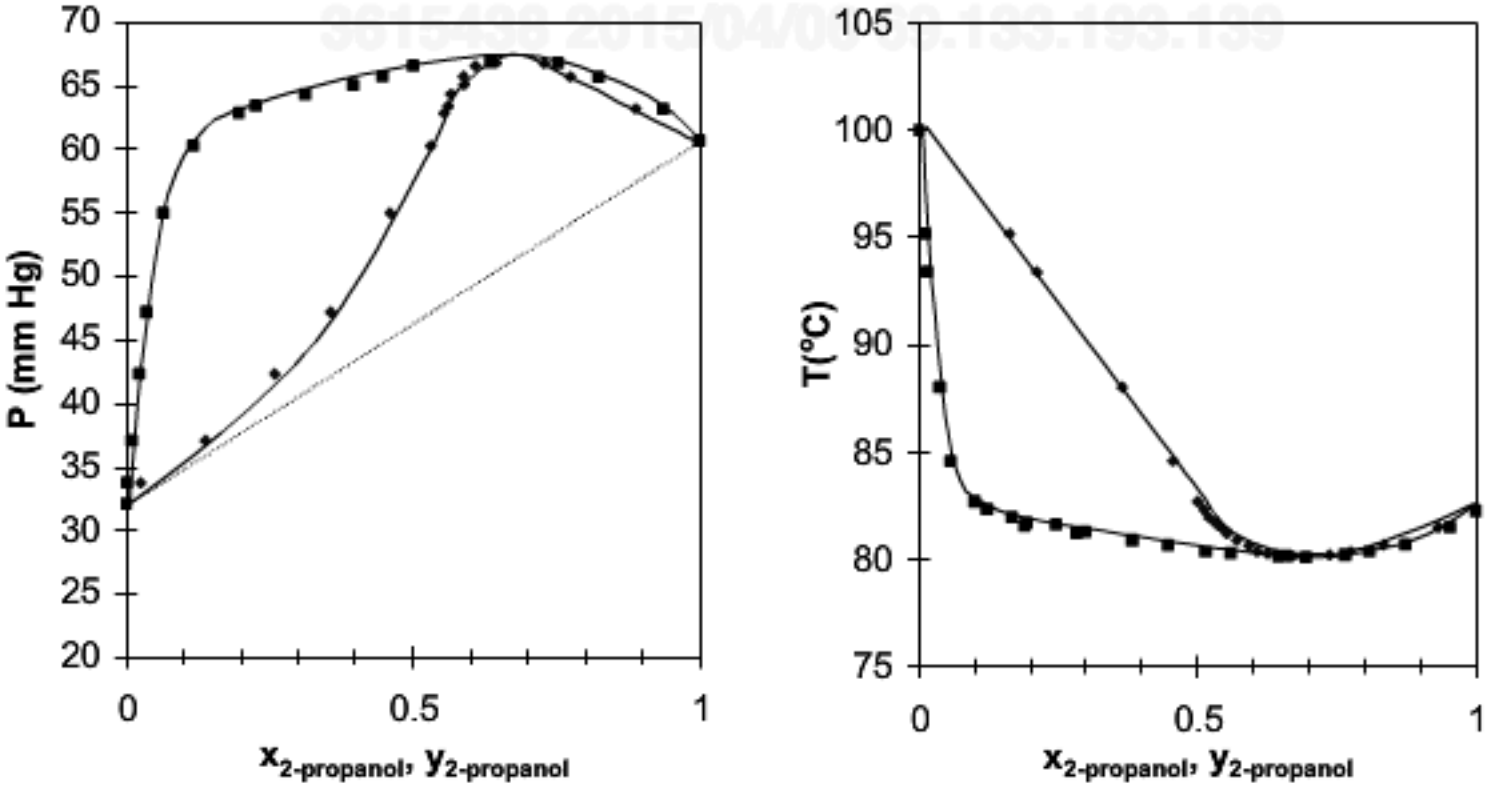
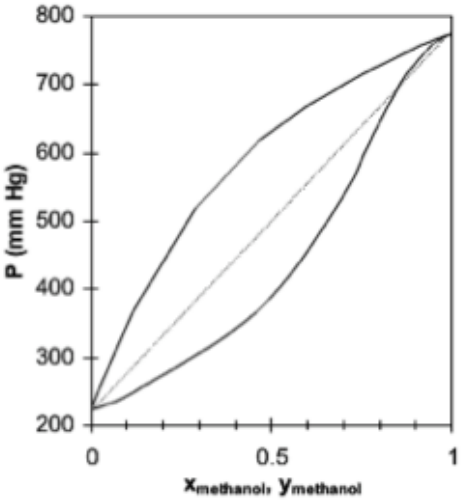


Figure 10.8 *(c), (d) Phase behavior of the 2-propanol + water system. Left figure at 30°C. Right figure at 760 mm Hg. (T-x-y from Wilson, A., Simons, E.L., 1952. Ind. Eng. Chem. 44:2214, P-x-y from Udovenko, V.V., and Mazanko. T.F. 1967. Zh. Fiz. Khim. 41:1615.)*

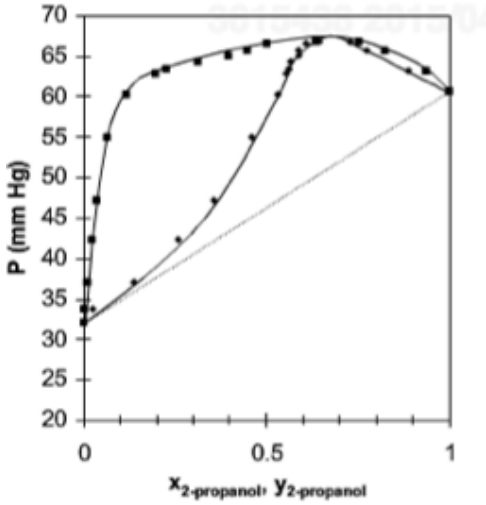
Positive deviations from Raoult's law. It is convenient to say that the components "dislike" each other.

In Fig. 10.8 the bubble line lies above the Raoult's law line, and these systems are said to have **positive deviations** from Raoult's law. Positive deviations occur when the components in the mixture would prefer to be near molecules of their own type rather than near molecules of the other component. Briefly, it is convenient to say that these components "dislike" each other. The 2-propanol + water system has vapor pressures that are close to each other relative to the deviation from ideality. As a result, the positive deviations are large enough to cause the pressure to reach a maximum (i.e,. $P^{max} > P_1^{sat} > P_2^{sat}$). The presence of a maximum (or minimum) causes the phase envelope to close at a composition known as the azeotropic composition. The nearness of the vapor pressures matters, because any deviation from ideality would give a maximum (or minimum), known as an **azeotrope,** if $P_1^{sat} = P_2^{sat}$. As a counterexample, the methanol + 3-pentanone system has significantly different vapor pressures for the components, and the deviations from ideality are not large enough to cause azeotrope formation. Recalling that the dew and bubble lines represent coexisting compositions at equilibrium, a maximum or minimum means that $x_i = y_i$ and relative volatility $\alpha_{ij} = 1$ at the azeotrope: $\alpha_{ij} > 1$ on one side of the azeotrope composition and $\alpha_{ij} < 1$ on the other side. This means that distillation ceases to provide separation at an azeotrope composition, and knowledge of azeotropes is critical for distillation design. When an azeotrope forms in a system with positive deviations, the azeotrope is a maximum on the *P-x-y* diagram and a minimum on the *T-x-y* diagram. To give a name to the type of azeotrope, the convention is to refer to azeotropes like that of 2-propanol + water as a **minimum boiling azeotrope,** referring to the boiling temperature reaching a minimum in composition. This can be confusing because the deviations from ideality are referred to as positive with respect to Raoult's Law on a *P-x-y* diagram. If you remember that "boiling" refers to boiling *temperature,* it may help you to reduce confusion. The azeotrope on a *P-x-y* diagram is a **maximum pressure azeotrope.** Since the vapor and liquid compositions are equivalent at the azeotrope, a flash drum or distillation column cannot separate a mixture at the azeotropic composition.

Relative volatility equals 1 for an azeotrope: $\alpha_{ij} > 1$ on one side of the azeotrope composition and $\alpha_{ij} < 1$ on the other side.



(*a*)



(*c*)

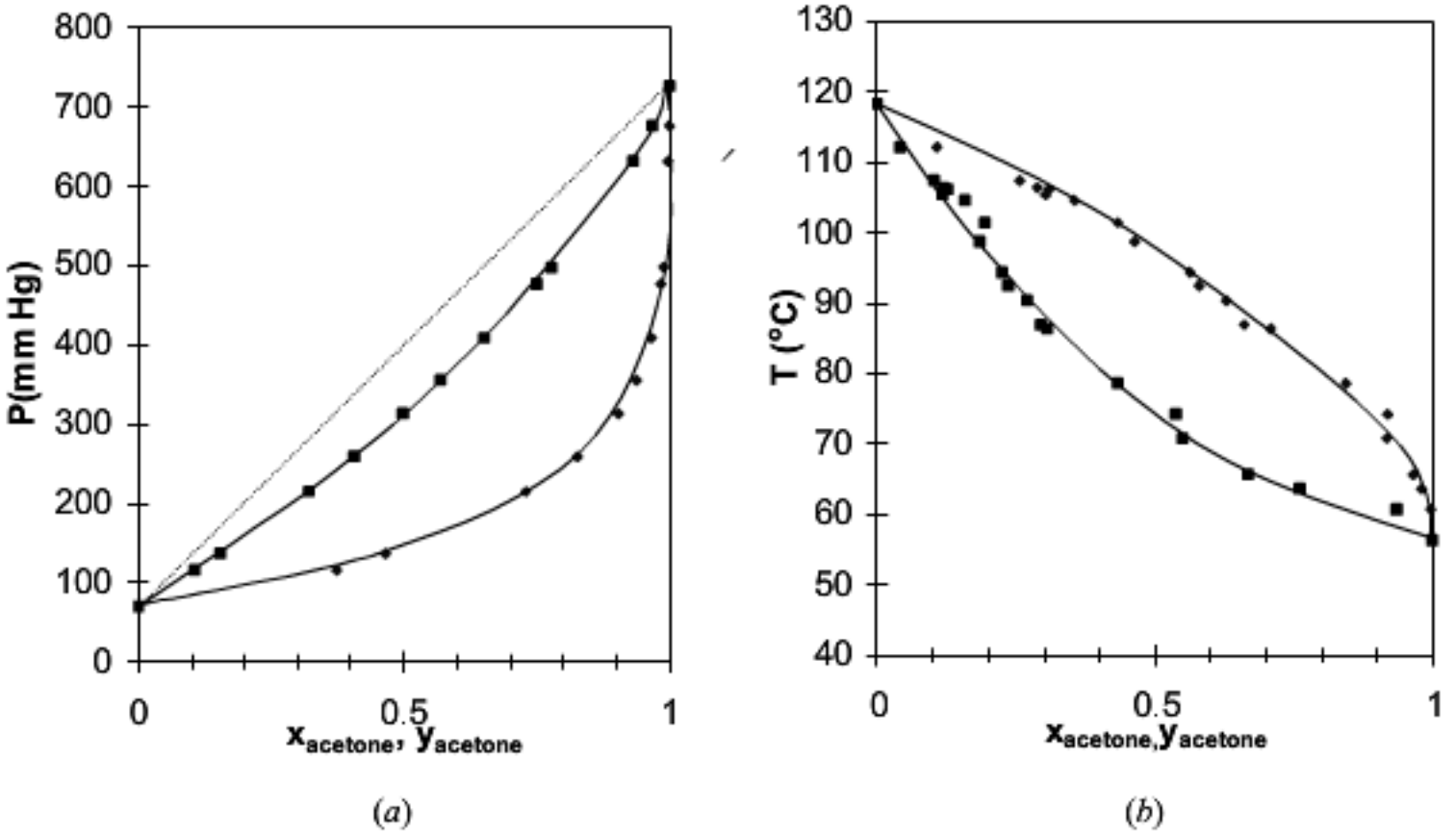


Figure 10.9 *(a), (b) Phase behavior of the acetone + acetic acid system. Left figure at 55°C. Right figure at 760 mm Hg. (T-x-y from York, R., Holmes, R.C. 1942. Ind. Eng. Chem. 34:345, P-x-y from Waradzin, W., Surovy, J., 1975. Chem. Zvesti 29:783.)*

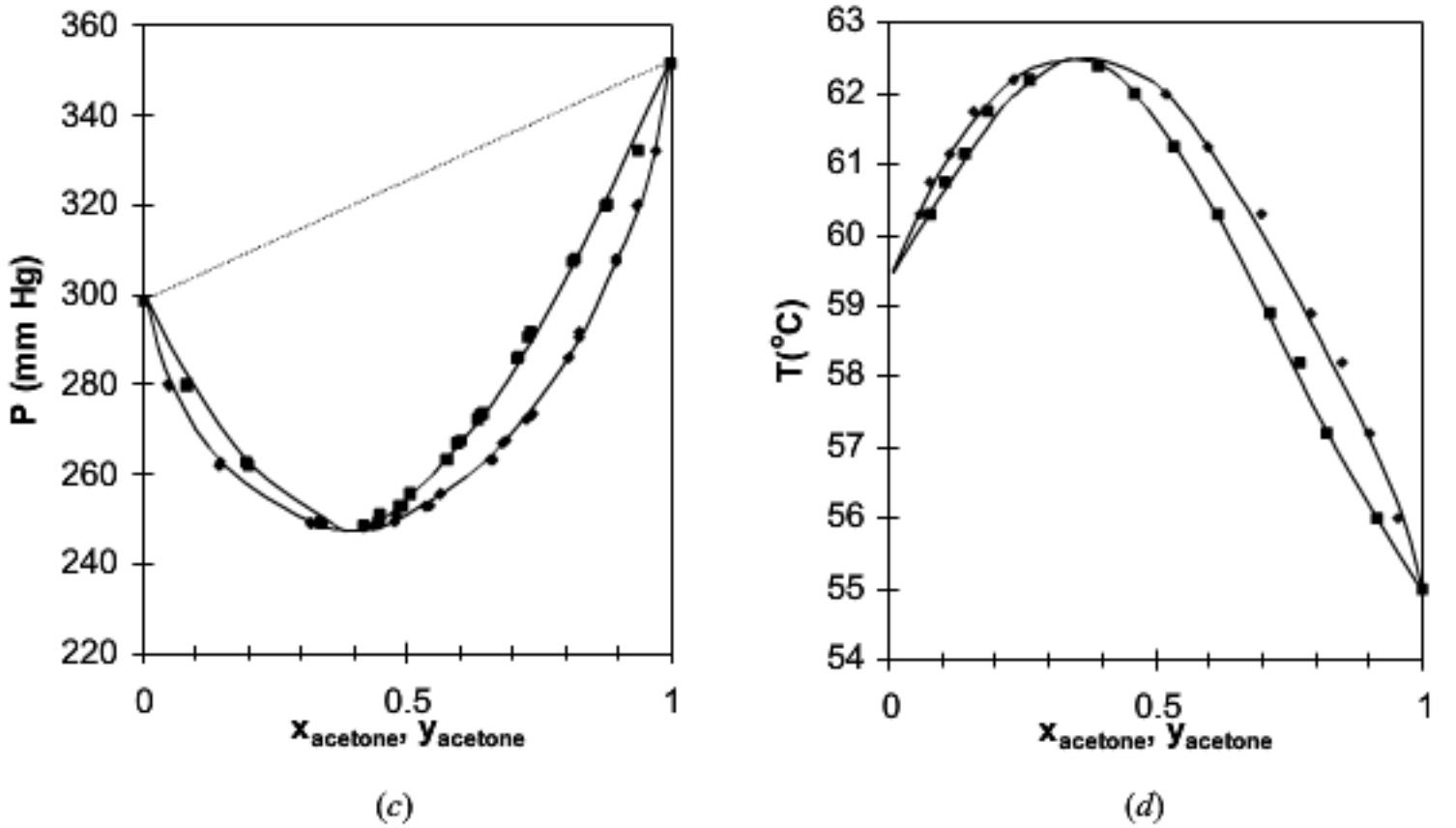
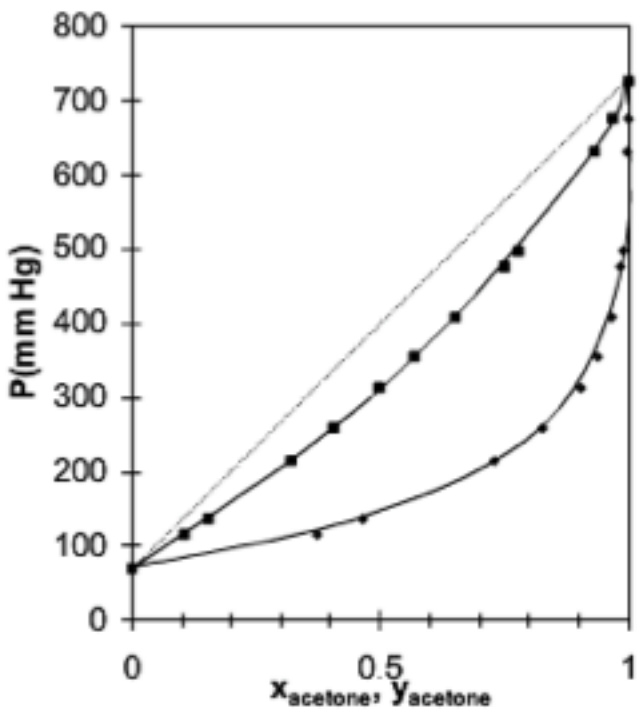


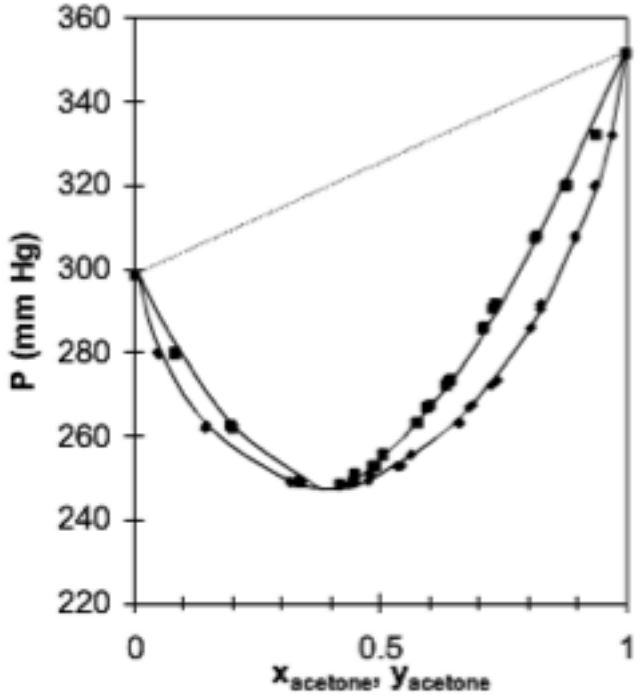
Figure 10.9 *(c); (d) Phase Behavior of the acetone + chloroform system. Left figure at 35.17°C. Right figure at 732 mm Hg. (T-x-y from Soday, F., Bennett, G.W., 1930. J.Chem. Educ. 7:1336, P-x-y from Zawidzki, V.J., 1900. Z. Phys. Chem. 35:129.)*

Negative deviations from Raoult's law. It is convenient to say that the components "like" each other.

In Fig. 10.9 the systems have **negative deviations** from Raoult's law because the bubble line lies below the Raoult's line. Similar azeotropic behavior is found in these systems if the vapor pressures are close to each other or the deviations are large. When an azeotrope forms in a system with negative deviations, the azeotrope is a minimum on the *P-x-y* diagram and a maximum on the *T-x-y* diagram. Therefore, this behavior is called a **maximum boiling azeotrope** or a **minimum pressure azeotrope.** From a chemical perspective, negative deviations indicate that the components "like" each other more than they like themselves. For example, mixing two acids may form an ideal solution, but mixing an acid with a base can give a negative deviation from ideality that feels warm to the touch. This is consistent with the negative sign on exothermic heats of reaction.



(*a*)



(*c*)

10.8 CONCEPTS FOR GENERALIZED PHASE EQUILIBRIA

$$d\underline{U}(T, P, n_1, n_2, \ldots n_i) = \left(\frac{\partial \underline{U}}{\partial P}\right)_{T,n} dP + \left(\frac{\partial \underline{U}}{\partial T}\right)_{P,n} dT + \sum_i \left(\frac{\partial \underline{U}}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \qquad 10.36$$

$$d\underline{G}(T, P, n_1, n_2, \ldots n_i) = \left(\frac{\partial \underline{G}}{\partial P}\right)_{T,n} dP + \left(\frac{\partial \underline{G}}{\partial T}\right)_{P,n} dT + \sum_i \left(\frac{\partial \underline{G}}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \qquad 10.37$$

These equations extend the use of calculus from Chapter 6 to composition variables.

At constant moles and composition of material, the mixture must follow the same constraints as a pure fluid. That is, the state is dependent on only two state variables *if we keep the composition constant.*

$$\Rightarrow (\partial \underline{G}/\partial P)_{T,n} = \underline{V} \quad \text{and} \quad (\partial \underline{G}/\partial T)_{P,n} = -\underline{S};$$

$$d\underline{G} = \underline{V}dP - \underline{S}dT + \sum_i \left(\frac{\partial \underline{G}}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \qquad 10.38$$

Chemical potential.

$$\boxed{\mu_i \equiv (\partial \underline{G}/\partial n_i)_{P,T,n_{j\neq i}}} \qquad 10.39$$

We commonly write

$$\boxed{d\underline{G} = \underline{V}dP - \underline{S}dT + \sum_i \mu_i dn_i} \qquad 10.40$$

Partial Molar Properties

: **partial molar Gibbs energy.** $\boxed{\mu_i \equiv (\partial \underline{G}/\partial n_i)_{P,\,T,\,n_{j\neq i}}}$ the **chemical potential,**

$$(\partial \underline{M}/\partial n_i)_{T,\,P,\,n_{j\neq i}} \equiv \overline{M}_i .$$

Partial molar quantities provide a mathematical way to assign the overall mixture property according to composition expressed in moles or mole fractions.

$$\boxed{\underline{M} = \sum_i n_i \overline{M}_i \quad \text{or} \quad M = \sum_i x_i \overline{M}_i} \qquad 10.41$$

As a result, we may write

$$\underline{G} = \sum_i n_i \overline{G}_i = \sum_i n_i \mu_i \text{ or } G = \sum_i x_i \overline{G}_i = \sum_i x_i \mu_i \qquad 10.42$$

Closed	Open	Natural Variables
$dU = TdS - PdV$	$d\underline{U} = Td\underline{S} - Pd\underline{V} + \sum_i \mu_i dn_i$	S,V
$dH = TdS + VdP$	$d\underline{H} = Td\underline{S} + \underline{V}dP + \sum_i \mu_i dn_i$	S,P
$dA = SdT - PdV$	$d\underline{A} = -\underline{S}dT - Pd\underline{V} + \sum_i \mu_i dn_i$	T,V
$dG = SdT + VdP$	$d\underline{G} = -\underline{S}dT + \underline{V}dP + \sum_i \mu_i dn_i$	T,P

Equilibrium Criteria

$$d\underline{G} = 0 \qquad \text{at equilibrium, for constant } T \text{ and } P \qquad 10.43$$

This equation applies to whatever system we define. Suppose we define our system to consist of two components (e.g,. EtOH + H_2O) distributed between two phases (e.g., vapor and liquid), $d\underline{G} = d\underline{G}^L + d\underline{G}^V = 0$, and at constant T and P, the moles may redistribute between the two phases, by Eqn. 10.40 for both phases:

$$d\underline{G}^L + d\underline{G}^V = \mu_1^L dn_1^L + \mu_2^L dn_2^L + \mu_1^V dn_1^V + \mu_2^V dn_2^V = 0$$

But if component 1 leaves the liquid phase then it must enter the vapor phase (and similarly for component 2) because the overall system is closed.

$$\Rightarrow dn_1^L = -dn_1^V \quad \text{and} \quad dn_2^L = -dn_2^V$$

$$\Rightarrow (\mu_1^V - \mu_1^L) dn_1^V + (\mu_2^V - \mu_2^L) dn_2^V = 0$$

The only way to make this equal to zero in general is:

$$\boxed{\mu_1^V = \mu_1^L \quad \text{and} \quad \mu_2^V = \mu_2^L} \qquad 10.44$$

The chemical potential of each component must be the same in each phase at equilibrium.

Setting the chemical potentials and T and P in each of the phases equal to each other provides a set of constraints (simultaneous equations) which may be solved for phase compositions provided

$$\left(\frac{\partial \underline{G}^L}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial \underline{G}^V}{\partial n_1}\right)_{T,P,n_2}; \left(\frac{\partial \underline{G}^L}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial \underline{G}^V}{\partial n_2}\right)_{T,P,n_1}; x_2 = 1 - x_1; y_2 = 1 - y_1;$$

which gives four equations with four unknowns (x_1, x_2, y_1, y_2) that we can solve, in principle.[11] The first two equations are simply the equivalency of chemical potentials in the two phases.

Chemical Potential of a Pure Fluid

The chemical potential of a pure fluid is simply the molar Gibbs energy.

$$\mu_{i,pure} = G_i \qquad 10.45$$

That is, the chemical potential of a pure fluid is simply the molar Gibbs energy. Pure components can be considered as a special case of the same general statement of the equilibrium constraint.

Component Fugacity

Fugacity is another way to express the chemical potential that is used more widely in engineering than chemical potential.

Let us generalize our pure component fugacity relations to apply to components in mixtures: At constant T, we defined $RTd\ln f \equiv dG$ (Eqn. 9.19) which can be generalized to define the fugacity of a component in a mixtures as

Carets (^) are used to denote component properties in mixtures for f while without a caret the property is the pure component f. When working with μ, the meaning is inferred from the context of the situation.

$$RTd\ln\hat{f}_i \equiv d\mu_i \qquad 10.46$$

Equality of Fugacities as Equilibrium Criteria

$$\boxed{\mu_i^V(T,P) = \mu_i^L(T,P)} \qquad 10.47$$

$$\mu_i^V - \mu_{i,pure} = RT\ln\frac{\hat{f}_i^V}{f_i} \qquad 10.48$$

$$\mu_i^V - \mu_i^L = RT\ln\left[\hat{f}_i^V/\hat{f}_i^L\right] = 0 \qquad 10.49$$

$$\boxed{\hat{f}_i^V = \hat{f}_i^L} \quad \text{at equilibrium.} \qquad 10.50$$

10.9 MIXTURE PROPERTIES FOR IDEAL GASES

We can now relate the mixing behavior to the partial molar properties. The partial molar quantities for ideal gases must be the same as the pure component properties.

$$\bar{V}_i^{ig} = V_i\,,\ \bar{U}_i^{ig} = U_i\,,\ \bar{H}_i^{ig} = H_i \qquad 10.51$$

$$\boxed{\underline{S}^{ig} = \sum_i n_i S_i^{ig} + \Delta\underline{S}_{mix} = \sum_i n_i S_i^{ig} - R\sum_i n_i \ln y_i} \text{ or } \boxed{S^{ig} = \sum_i y_i S_i^{ig} - R\sum_i y_i \ln y_i} \quad \text{(ig) } 10.52$$

Therefore, the entropy of mixing is nonzero and positive:

$$\boxed{\Delta S_{mix}^{ig} = S^{ig} - \sum_i y_i S_i^{ig} = -R\sum_i y_i \ln y_i > 0} \qquad \text{(ig) } 10.53$$

and the partial molar entropy is

$$\bar{S}_i^{ig} = S_i^{ig} - R\ln y_i \qquad 10.54$$

The Gibbs energy and the fugacity will be at the core of phase equilibria calculations. The Gibbs energy of an ideal gas is obtained from the definition, $G \equiv H - TS$. Using H^{ig} an S^{ig} from above,

$$\underline{G}^{ig} \equiv \underline{H}^{ig} - T\underline{S}^{ig} = \sum_i n_i H_i^{ig} - T\left(\sum_i n_i S_i^{ig} - R\sum_i n_i \ln y_i\right) = \sum_i n_i G_i^{ig} + RT\sum_i n_i \ln y_i \quad \text{(ig) 10.55}$$

Therefore, the Gibbs energy of mixing is nonzero and negative:

$$\Delta G_{mix}^{ig} = G^{ig} - \sum_i y_i G_i^{ig} = R\sum_i y_i \ln y_i < 0 \quad \text{(ig) 10.56}$$

$$\mu_i^{ig} = (\partial \underline{G}^{ig}/\partial n_i)_{T,\,P,\,n_{j\neq i}} = G_i^{ig} + RT\left(\partial\left(\sum_i n_i \ln y_i\right)/\partial n_i\right)_{T,\,P,\,n_{j\neq i}} \quad \text{(ig) 10.57}$$

The derivative is most easily seen by expanding the logarithm before differentiation, $\ln y_i = \ln n_i - \ln n$. Then,

$$\left(\partial\left(\sum_i n_i \ln n_i - \ln n \sum_i n_i\right)/\partial n_i\right)_{T,\,P,\,n_{j\neq i}} = \ln n_i + 1 - 1 - \ln n = \ln y_i \quad 10.58$$

Therefore, we find the **chemical potential of an ideal-gas component:**

$$\mu_i^{ig} = G_i^{ig} + RT\ln y_i \quad \text{(ig) 10.59}$$

$$\mu_i^{ig} - \mu_{i,pure}^{ig} = RT\ln\frac{\hat{f}_i^{ig}}{f_{i,pure}^{ig}} = RT\ln y_i \text{ or } \hat{f}_i^{ig} = y_i f_{i,pure}^{ig} \qquad \text{(ig) 10.60}$$

By Eqn. 9.22, $f_{pure}^{ig} = P$, resulting in the **fugacity of an ideal-gas component:**

$$\boxed{\hat{f}_i^{ig} = y_i P} \qquad \text{(ig) 10.61}$$

Therefore, the fugacity of an ideal-gas component is simply its **partial pressure,** $y_i P$. This makes the ideal-gas fugacity easy to quantify rapidly for engineering purposes. One of the goals of the calculations that will be pursued in Chapter 15 is the quantification of the deviations of the fugacity from ideal-gas values quantified by the component fugacity coefficient.

The fugacity of a component in an ideal-gas mixture is particularly simple; it is equal to the $y_i P$, the partial pressure!

10.10 MIXTURE PROPERTIES FOR IDEAL SOLUTIONS

$$\frac{\Delta S_{mix}^{is}}{R} = -\sum_i x_i \ln x_i \qquad 10.63$$

The entropy of mixing is *nonzero* for an ideal solution.

$$\frac{\Delta G_{mix}^{is}}{RT} = \frac{\Delta H_{mix}^{is}}{RT} - \frac{\Delta S_{mix}^{is}}{R} = \sum_i x_i \ln x_i \qquad 10.65$$

$$\Delta G_{mix} \equiv G - \sum_i x_i G_i \qquad 10.66$$

$$\frac{\Delta G_{mix}}{RT} = \sum x_i \frac{(\mu_i - G_i)}{RT} = \sum x_i \ln\left(\frac{\hat{f}_i}{f_i}\right) \qquad 10.67$$

$$\frac{\Delta G_{mix}}{RT} = \sum_i x_i \ln x_i = \sum_i x_i \ln\left(\frac{\hat{f}_i}{f_i}\right)$$

By comparing the relations in the logarithms, we obtain the **Lewis-Randall rule** for ideal solutions:

$$\hat{f}_i^{is}/f_i = x_i \quad \Rightarrow \quad \hat{f}_i^{is} = x_i f_i \qquad 10.68$$

Lewis-Randall rule for component fugacity in an ideal solution.

10.11 THE IDEAL SOLUTION APPROXIMATION AND RAOULT'S LAW

By our equilibrium constraint,

$$\hat{f}_i^V = \hat{f}_i^L \tag{10.69}$$

By our ideal solution approximation in both phases, the equilibrium criteria becomes

$$\boxed{y_i f_i^V = x_i f_i^L} \tag{10.70}$$

Now we need to substitute the expressions for f_i^V and f_i^L that we developed in Chapter 9. The fugacity of the pure vapor comes from Eqn. 9.25:

$$f_i^V = \varphi_i^V P \tag{10.71}$$

The fugacity of the liquid comes from Eqn. 9.39:

$$f_i^L = \varphi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^L (P - P_i^{sat})}{RT}\right) \tag{10.72}$$

Combining Eqns. 10.70–10.72,

$$y_i \varphi_i^V P = x_i \varphi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^L (P - P_i^{sat})}{RT}\right)$$

Writing in terms of the K_i ratio,

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P}\left[\frac{\varphi_i^{sat} \exp[V_i^L (P - P_i^{sat})/RT]}{\varphi_i^V}\right]$$

Note: *at reasonably low pressures,*

$$\frac{\varphi_i^{sat}}{\varphi_i} \approx 1, \text{ and } \exp[V_i^L (P - P_i^{sat})/RT] \approx 1$$

resulting in Raoult's Law,

$$\boxed{K_i = \frac{P_i^{sat}}{P}} \quad \text{or} \quad \boxed{y_i P = x_i P_i^{sat}} \qquad 10.73$$

Raoult's law.