## Henry's Law

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

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

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

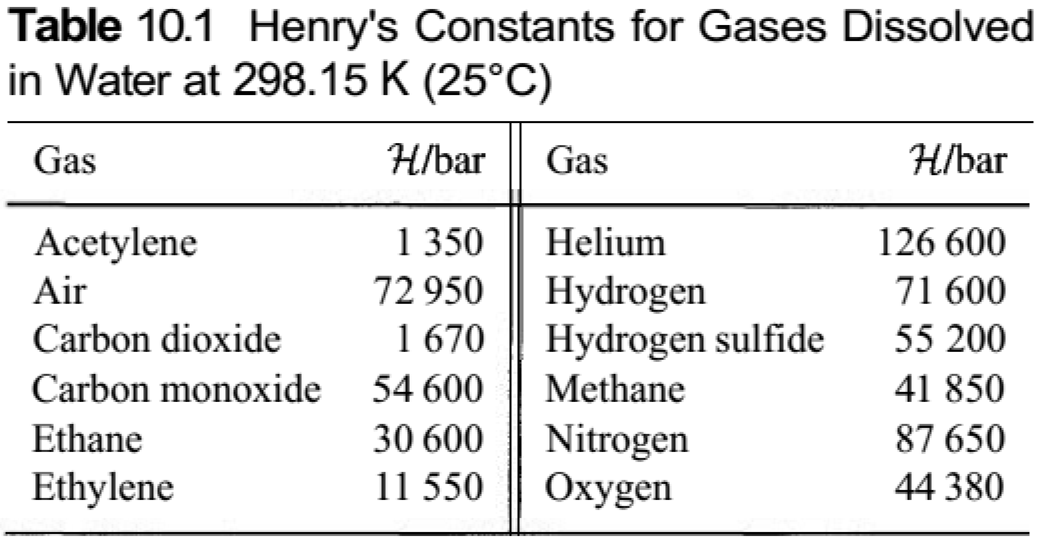


**Table 10.1** Henry's Constants for Gases Dissolved in Water at 298.15 K (25°C)

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

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

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

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

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

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

Assuming that carbonated water contains only $CO_2$(1) and $H_2O$(2), determine the compositions of the vapor and liquid phases in a sealed can of "soda" and the pressure exerted on the can at 10°C. Henry's constant for $CO_2$ in water at 10°C is about 990 bar.

## Solution 10.2

As a matter of course, one should always heed whatever insight the phase rule may provide with respect to the solution of an equilibrium problem. Application of the phase rule to this 2-phase, 2-species system yields $F = 2$. However, only the temperature is given in the problem statement, and a further intensive variable must be specified if the problem is to have a unique solution. The liquid-phase mole fraction of $CO_2$ is an appropriate additional variable, and for a particular value of $x_1$ the problem has a particular solution. We illustrate with $x_1 = 0.01$.

Henry's law for species 1 and Raoult's law for species 2 are written:

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

These equations sum to give:

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

With $\mathcal{H}_1 = 990$ bar and $P_2^{sat} = 0.01227$ bar (from the steam tables at 10°C),

$$P = (0.01)(990) + (0.99)(0.01227) = 9.912 \text{ bar}$$

Then by Raoult's law, Eq. (10.1) written for species 2:

$$y_2 = \frac{x_2 P_2^{sat}}{P} = \frac{(0.99)(0.01227)}{9.912} = 0.0012$$

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

## 10.5 VLE BY MODIFIED RAOULT'S LAW

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

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

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

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

$$P = \sum x_i \gamma_i P_i^{\text{sat}} \tag{10.6}$$

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

$$P = \frac{1}{\sum y_i / \gamma_i P_i^{\text{sat}}} \tag{10.7}$$

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

$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2 \qquad \text{where} \qquad A = 2.771 - 0.00523\,T$$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{sat} = 16.59158 - \frac{3{,}643.31}{T - 33.424} \qquad \ln P_2^{sat} = 14.25326 - \frac{2{,}665.54}{T - 53.424}$$

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

(*a*) $P$ and $\{y_i\}$, for $T = 318.15$ K and $x_1 = 0.25$.

(*b*) $P$ and $\{x_i\}$, for $T = 318.15$ K and $y_1 = 0.60$.

(*c*) $T$ and $\{y_i\}$, for $P = 101.33$ kPa and $x_1 = 0.85$.

(*d*) $T$ and $\{x_i\}$, for $P = 101.33$ kPa and $y_1 = 0.40$.

(*e*) The azeotropic pressure, and the azeotropic composition, for $T = 318.15$ K.

## Solution 10.3

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

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

Activity coefficients are calculated from the correlating equations:

$$A = 2.771 - (0.00523)(318.15) = 1.107$$

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

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

The pressure is given by Eq. (10.6):

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

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

$$y_1 = 0.282 \qquad y_2 = 0.718$$

$P_2^{sat}$, and $A$ are unchanged. However, the liquid-phase composition is here unknown, but is required in the calculation of activity coefficients. An iterative procedure is indicated; initial values are provided by Raoult's law, for which $\gamma_1 = \gamma_2 = 1.0$. The required steps, with current values of $\gamma_1$ and $\gamma_2$, are:

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

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

- Calculate $x_1$ by Eq. (10.5):

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

- Evaluate activity coefficients; return to the first step.

Iteration to convergence on a value for $P$ leads to final values:

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

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

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

Application for $P = 101.33$ kPa leads to:

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

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

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

An iterative procedure consists of the steps:

- For the current value of $T$ calculate values for $A$, $\gamma_1$, $\gamma_2$, and $\alpha \equiv P_1^{sat}/P_2^{sat}$ from the given equations.
- Find a new value for $P_1^{sat}$ from Eq. (10.6) written:

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

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

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

Iteration to convergence on a value for $T$ yields final values:

$$T = 331.20\text{ K} \qquad P_1^{sat} = 95.24\text{ kPa} \qquad P_2^{sat} = 48.73\text{ kPa}$$

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

The vapor-phase mole fractions are given by:

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

(*d*) A *DEW T* calculation. Because $P = 101.33$ kPa, the saturation temperatures are the same as those of part (*c*), and an initial value for the unknown temperature is found as a mole-fraction weighted average of these values:

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

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

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

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

- Calculate values of $\gamma_1$ and $\gamma_2$ from the correlating equations.
- Find a new value for $P_1^{sat}$ from Eq. (10.7) written:

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

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

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

- Return to the initial step and iterate with the current values of $\gamma_1$ and $\gamma_2$ until the process converges on a value of $T$.

$A = 1.0624 \qquad \gamma_1 = 1.3629 \qquad \gamma_2 = 1.2523$

$x_1 = 0.4602 \qquad x_2 = 0.5398$

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

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

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

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

Therefore,

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

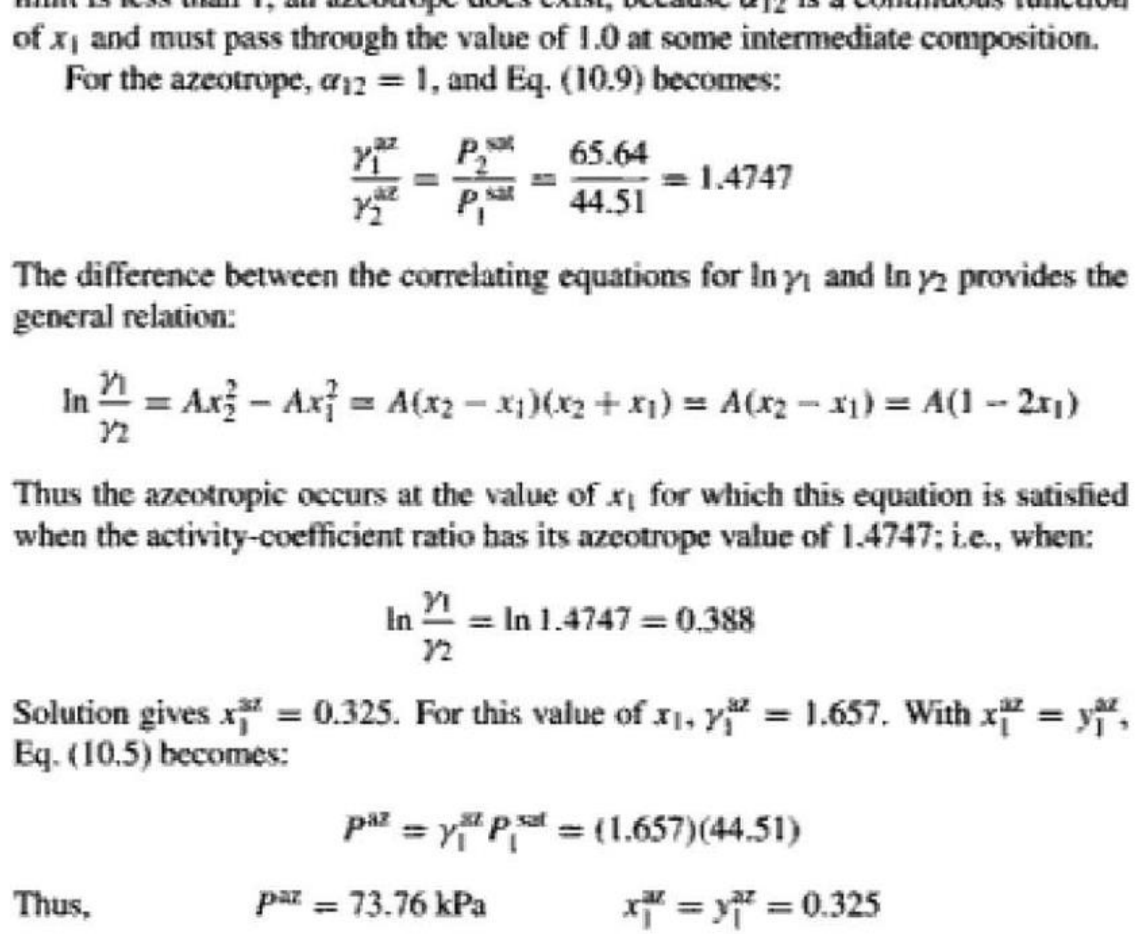
The correlating equations for the activity coefficients show that when $x_1 = 0$, $\gamma_2 = 1$, and $\gamma_1 = \exp(A)$; when $x_1 = 1$, $\gamma_1 = 1$ and $\gamma_2 = \exp(A)$. Therefore in these limits,

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

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

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

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



of $x_1$ and must pass through the value of 1.0 at some intermediate composition.

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

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

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

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

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

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

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

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

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

Dewpoint and bubblepoint calculations are readily made with software packages such as Mathcad@ and Maple@, in which iteration is an integral part of an equation-solving routine. Mathcad programs for solution of Ex. 10.3, parts (a) through (d), are given in App. D.2. Calculations for multicomponent systems made without simplifying assumptions are readily carried out in like manner by computer. The procedures are presented in Sec. 14.1

## 10.6 VLE FROM K-VALUE CORRELATIONS

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

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

This quantity is usually called simply a K-value. Although it adds nothing to thermodynamic knowledge of VLE, it does serve as a measure of the "lightness" of a constituent species, i.e., of its tendency to favour the vapour phase. When Ki is greater than unity, species i exhibits a higher concentration in the vapour phase; when less, a higher concentration in the liquid phase, and is considered a "heavy" constituent. Moreover, the use of K-values makes for computational convenience, allowing elimination of one set of mole fractions.{yi} or {xi) in favour of the other.

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

$$K_i = \frac{P_i^{\text{sat}}}{P} \qquad (10.11)$$

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

$$K_i = \frac{\gamma_i P_i^{\text{sat}}}{P} \qquad (10.12)$$

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

$$\sum_i K_i x_i = 1 \qquad (10.13)$$

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

$$\sum_i \frac{y_i}{K_i} = 1 \qquad (10.14)$$

Equations (10.1 1) and (10.12) together with Eq. (10.10) represent alternative forms of Raoult's law and modified Raoult's law. The great attraction of Raoult's law is that it expresses K-values as functions of just T and P, independent of the compositions of the liquid and vapour phases. Where the assumptions which underlie Raoult's law are appropriate, this allows K-values to be calculated and correlated as functions of T and P. For mixtures of light hydrocarbons and other simple molecules, in which the molecular force fields are relatively uncomplicated, correlations of this kind have approximate validity. Figures 10.13 and 10.14, show monographs for the K-values of light hydrocarbons as functions of T and P, prepared by Dadyburjor[7]. They do allow for an average effect of composition, but the essential basis is Raoult's law.

## Flash Calculations

An important application of VLE is the ***flash calculation***. The name originates from the fact that a liquid at a pressure equal to or greater than its bubblepoint pressure "flashes" or partially evaporates when the pressure is reduced, producing a two-phase system of vapour and liquid in equilibrium.

We consider here only the P, T-flash, which refers to any calculation of the quantities and compositions of the vapour and liquid phases making up a two-phase system in equilibrium at known T, P, and overall composition.

Consider a system containing one mole of nonreacting chemical species with an overall composition represented by the set of mole fractions {zi }. Let ***L*** be the moles of liquid, with mole fractions {xi}, and let ***V*** be the moles of vapour, with mole fractions {yi}. The material-balance equations are:

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

$$z_i = x_i\, L + y_i\, V \qquad (\text{ i=1,2,3……….N})$$

Combining these equations to eliminate ***L*** gives:

$$z_i = x_i\,(1-V) + y_i\, V \qquad (\text{ i=1,2,3……….N}) \qquad (10\text{-}15)$$

Substituting xi = yi / Ki , and solving for yi yields:

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

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

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

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

### Example 10.5

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

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

## Solution 10.3

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

$$\begin{aligned} P_{\text{bubl}} &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}} \\ &= (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) = 132.40 \text{ kPa} \end{aligned}$$

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

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

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

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

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

Substitute known values into Eq. (10.17):

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

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

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

Whence,

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

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

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

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

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

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