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.[6]

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

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

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

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

---

## Example 10.3

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:

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

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.

[6]The correlation of activity-coefficient data is treated in Secs. 12.1 and 12.2.

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## 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:

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

$$\gamma_1 = \exp(Ax_2^2) = \exp\left[(1.107)(0.75)^2\right] = 1.864$$

$$\gamma_2 = \exp(Ax_1^2) = \exp\left[(1.107)(0.25)^2\right] = 1.072$$

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

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

(*b*) A *DEW P* calculation. With $T$ unchanged from part (*a*), the values of $P_1^{sat}$, $P_2^{sat}$, 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:

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

- Return to the initial step.

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 $P_1^{\text{sat}}$ from Eq. (10.7) written:

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

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

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

- 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 $T$.

The process yields the final values:

| | | |
|---|---|---|
| $T = 326.70$ K | $P_1^{\text{sat}} = 64.63$ kPa | $P_2^{\text{sat}} = 90.89$ kPa |
| $A = 1.0624$ | $\gamma_1 = 1.3629$ | $\gamma_2 = 1.2523$ |
| $x_1 = 0.4602$ | $x_2 = 0.5398$ | |

(*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),

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

Therefore,

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

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,

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

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

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

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

Because the value at one limit is greater than 1, whereas the value at the other limit is less than 1, an azeotrope does exist, because $\alpha_{12}$ is a continuous function 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, $\quad P^{az} = 73.76 \text{ kPa} \qquad x_1^{az} = y_1^{az} = 0.325$

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 $K_i$, defined as:

$$\boxed{K_i \equiv \frac{y_i}{x_i}} \tag{10.10}$$

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 favor the vapor phase. When $K_i$ is greater than unity, species $i$ exhibits a higher concentration in the vapor phase; when less, a higher concentration in the liquid phase, and