

ChE Thermodynamics Problems

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Chapter 10

Example 10.1*

Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{\text{sat}}/\text{kPa} = 14.2724 - \frac{2945.47}{T - 49.15}$$
$$\ln P_2^{\text{sat}}/\text{kPa} = 14.2043 - \frac{2972.64}{T - 64.15}$$

- (a) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 75 °C.
- (b) Prepare graph showing t vs. x_1 and t vs. y_2 for a pressure of 70 kPa.

Solution:

- (a)

$$P_\alpha = x_\alpha P_\alpha^*$$

Substitute this to the Antoine equation:

$$\ln \frac{P_\alpha/\text{kPa}}{x_\alpha} = A_\alpha - \frac{B_\alpha}{t/^\circ\text{C} + C_\alpha}$$
$$P = P_1^{\text{sat}} x_1 + P_2^{\text{sat}} (1 - x_1)$$
$$y_\alpha = \frac{P_\alpha}{P} = \frac{P_\alpha^{\text{sat}} x_\alpha}{P}$$

The plot is shown in Figure (1)

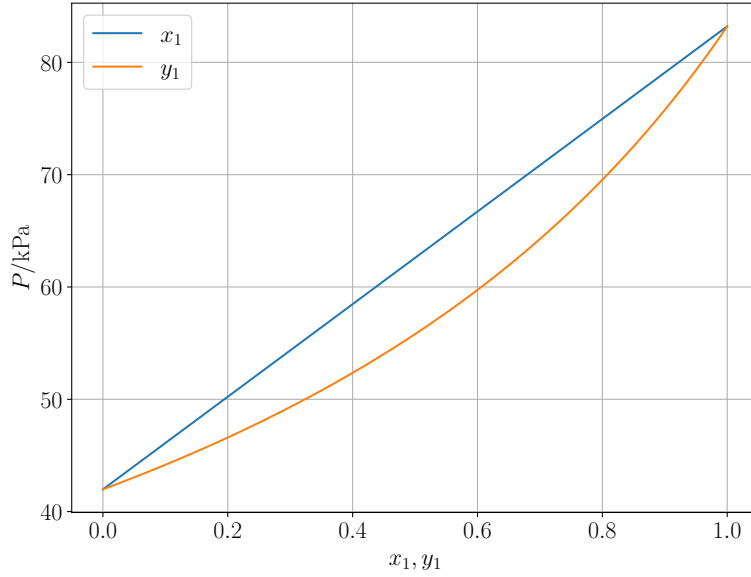


Figure 1: Plot of pressure versus liquid and vapor mole fraction of component 1 as described in Example 10.1a*

(b) This is another form of the Antoine equation:

$$T_{\alpha}^{\text{sat}} = \frac{B_{\alpha}}{A_{\alpha} - \ln P} + C_{\alpha}$$

Solve for T_1^{sat} and T_2^{sat} as these comprise of the range of the graph. Solve for:

$$\ln P_{\alpha}^{\text{sat}} = A_{\alpha} - \frac{B_{\alpha}}{T + C_{\alpha}}$$

To solve for:

$$x_1 = \frac{P - P_2^{\text{sat}}}{P_1^{\text{sat}} - P_2^{\text{sat}}}$$

Which is derived from:

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

The plot is shown in Figure (2)

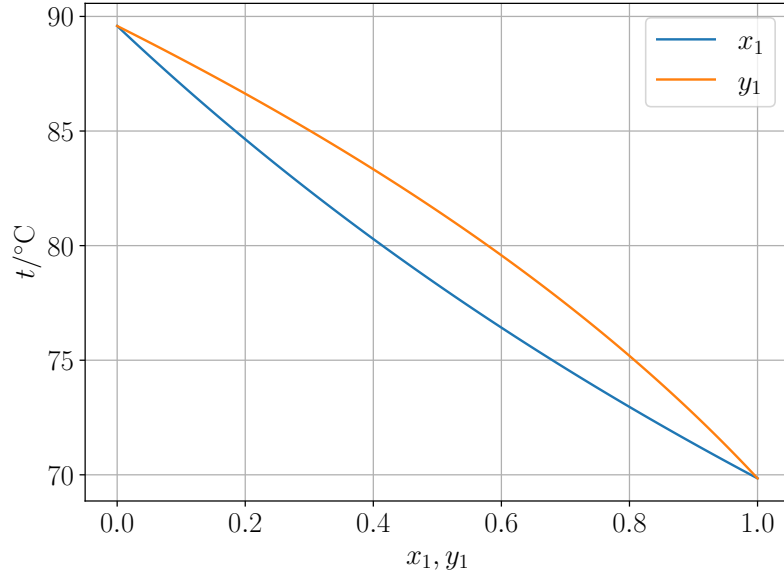


Figure 2: Plot of temperature (in $^\circ\text{C}$) versus liquid and vapor mole fraction of component 1 as described in Example 10.1b*

Example 10.2*

Assuming that carbonated water contains only $\text{CO}_2(1)$ and $\text{H}_2\text{O}(2)$, 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 (283.15 K). Henry's constant for CO_2 in water at 10°C (283.15 K) is about 990 bar **Solution:**

Applying the phase rule:

$$F = 2 - \pi + N$$

$$F = 2$$

Only the temperature of the system is given. We must give another intensive variable. And since we are given the Henry's constant it is good that we limit the amount of C_{02} in the liquid, $x_1 = 0.01$.

$$\begin{aligned} y_1 P &= x_1 \mathcal{H}_1 & y_2 P &= x_2 P_2^{\text{sat}} \\ P &= x_1 \mathcal{H}_1 + x_2 P_2^{\text{sat}} \end{aligned}$$

The value of P_2^{sat} can be found at the steam table, at 10 °C, which is 0.01227 bar

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

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

$$y_1 = \boxed{0.9988}$$

Example 10.3*

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

$$\ln y_1 = Ax_2^2 \quad \ln y_2 = Ax_1^2 \text{ where } A = 2.771 - 0.00523T$$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{\text{sat}} = 16.59158 - \frac{3643.31}{T - 33.424}$$

$$\ln P_2^{\text{sat}} = 14.25326 - \frac{2665.54}{T - 53.424}$$

where T is in kelvins and the vapor pressures are in kPa. Assuming the validity of Eq (1), calculate

- P and $\{y_i\}$, for $t/T = 45 \text{ °C}/318.15 \text{ K}$ and $x_1 = 0.25$
- P and $\{x_i\}$, for $t/T = 45 \text{ °C}/318.15 \text{ K}$ and $y_i = 0.60$
- T and $\{y_i\}$, for $P = 101.33 \text{ kPa}$ and $y_i = 0.85$
- T and $\{x_i\}$, for $P = 101.33 \text{ kPa}$ and $y_i = 0.40$
- The azeotropic pressure, and the azeotropic composition, for $t/T = 45 \text{ °C}/318.15 \text{ K}$

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (i = 1, 2, \dots, N) \quad (1)$$

Solution:

- Solve for the activity coefficients:

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

$$\gamma_1 = \exp(Ax_2^2) = 1.864$$

$$\gamma_2 = \exp(Ax_1^2) = 1.072$$

And then for pressure:

$$P = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}$$

$$P = \boxed{73.50 \text{ kPa}}$$

And then for the vapor mole fractions:

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

$$y_1 = 0.281$$

$$y_2 = 0.719$$

(b)