

1 Phase Equilibria [1]

Vapor-liquid equilibrium (VLE) is the state of coexistence between liquid and vapor phases. For a one component system, this is easily visualized, as shown in Figure 1. As the number

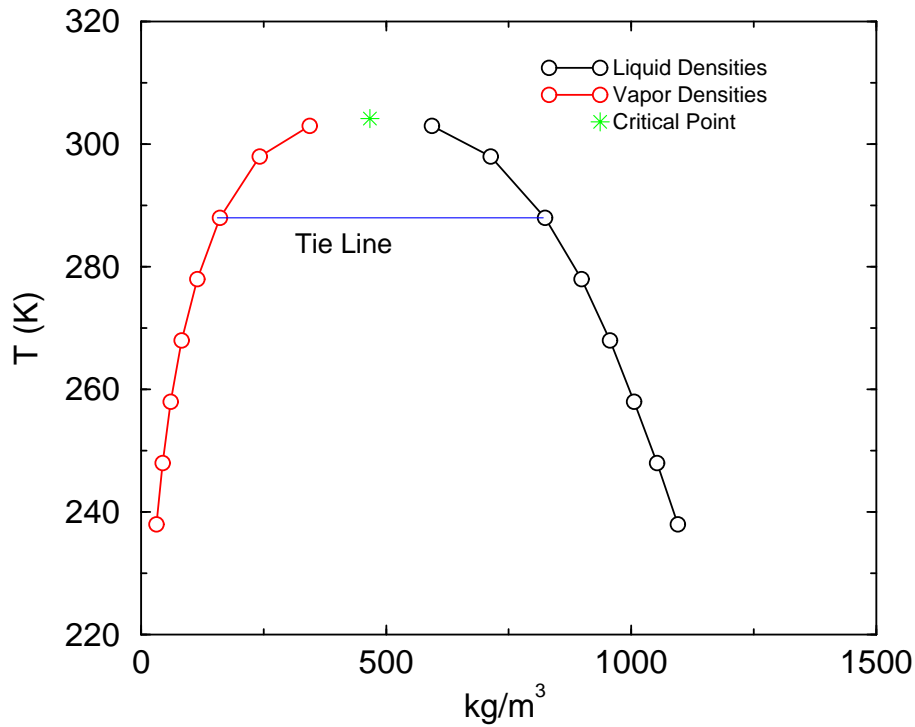


Figure 1: Vapor-liquid coexistence curve for CO_2 [2].

of components increase, so does the complexity of the phase diagram. Binary systems are usually represented as slices of the three-dimensional phase diagram, taken either at constant temperature or pressure. In Figure 2, an example of a pressure-composition diagram is presented for the mixture CO_2 /propane at 294.15K. Three component systems are represented graphically by taking slices of the four-dimensional VLE surface at constant temperature and pressure. An example of this is shown for the system CO_2 /propane/ N_2 at 270 K and 60 bar in Figure 3. For reasons of complexity, systems of four or more components are not usually represented graphically.

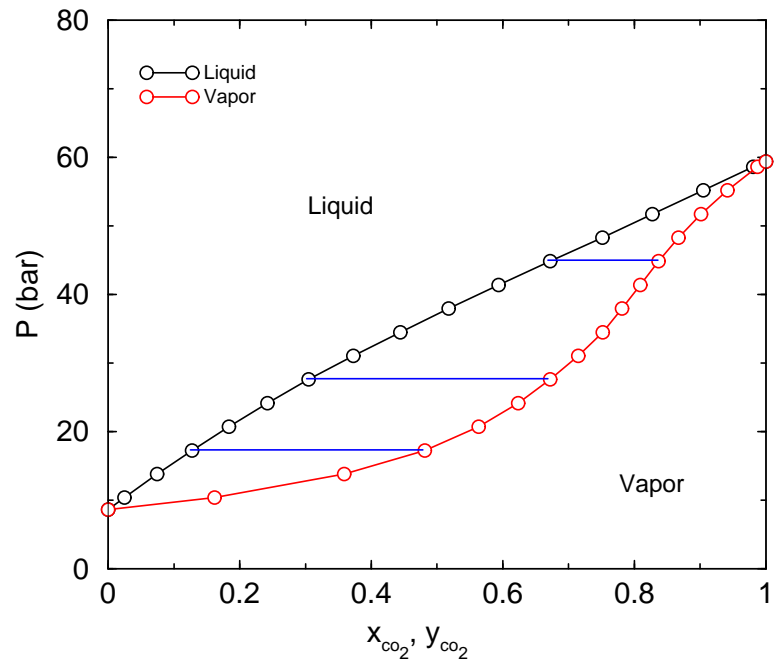


Figure 2: Pressure-composition diagram for a mixture of CO₂(1)/propane(2) at 294.15K [3].

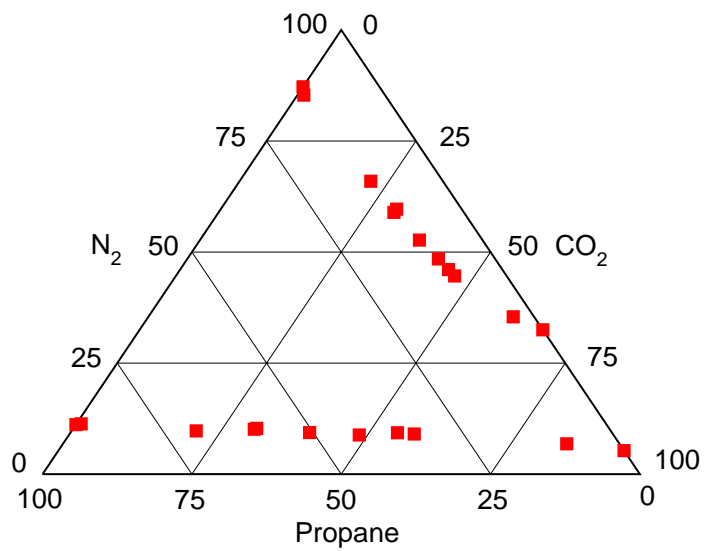


Figure 3: Pressure-composition diagram for a mixture of CO₂(1)/propane(2)/N₂(3) at 270K and 60 bar [4].

2 Gibbs Phase Rule

For any system at equilibrium, the number of independent variables required to fix its intensive state is given by:

$$F = 2 - \pi + N \quad (1)$$

where π is the number of phases, N is the number of components and F is known as the “degrees of freedom” of the system.

Definitions

- **Phase:** A homogeneous region of matter.
- **Intensive property:** A property that is independent of system size.
 - Ex. Temperature, pressure, density
- **Extensive property:** A property that depends on system size.
 - Ex. Mass, volume.

3 Raoult's Law

Raoult's law relates the composition of the vapor and liquid phases that are in equilibrium with each other through the vapor pressure and the total system pressure. The two major assumptions of Raoult's Law are:

- The vapor phase behaves as an ideal gas.
- The liquid phase behaves as an ideal solution.

NOTE: Raoult's may not be applied for systems where the vapor and liquid phases are not in equilibrium with each other. Raoult's law is:

$$p_i = y_i P = x_i p_i^* \quad (2)$$

where y_i is the mole fraction of component i in the gas phase, x_i is the mole fraction of component i in the liquid phase, p_i^* is the vapor pressure of component i , P is the total system pressure and p_i is the partial pressure of component i .

Since the total system pressure P is equal to the sum of the partial pressures p_i , we can derive the following expression:

$$P = x_1 p_1^* + x_2 p_2^* + \dots + x_n p_n^* \quad (3)$$

Combining equations 2 and 3 gives the following useful expression:

$$\frac{y_1 P}{p_1^*} + \frac{y_2 P}{p_2^*} + \dots + \frac{y_n P}{p_n^*} = 1 \quad (4)$$

A simple rearrangement of equation 4 yields:

$$P = \frac{1}{\frac{y_1}{p_1^*} + \frac{y_2}{p_2^*} + \dots + \frac{y_n}{p_n^*}} \quad (5)$$

With these equations, it is possible to perform a variety of calculations, which are listed in the table below

Quantities given	Calculate	Calculation type
x_i, T	y_i, P	bubble pressure
y_i, T	x_i, P	dew pressure
x_i, P	y_i, T	bubble temperature
y_i, P	x_i, T	dew temperature

4 Example #1: An application of Raoult's law

Suppose we have a binary mixture of acetonitrile(1) and nitromethane(2). The vapor pressures of each component are given by the following relationships

$$\ln p_1^* = 14.2724 - \frac{2945.47}{T + 224.00} \quad (6)$$

and

$$\ln p_2^* = 14.2043 - \frac{2972.64}{T + 209.00} \quad (7)$$

where T is in $^{\circ}\text{C}$ and p_i^* is in kPa.

A. Prepare a graph of P vs. x_1 and P vs. y_1 for $T = 75^{\circ}\text{C}$.

B. Prepare a graph of T vs. x_1 and t vs. y_1 for $P = 70$ kPa.

4.1 $P - x - y$ Calculations

To get the P vs. x_1 leg of the phase diagram, a bubble pressure calculation is required.

$$P = x_1 p_1^* + x_2 p_2^* \quad (8)$$

Remember: $x_2 = 1 - x_1$. Substitution into 8 gives:

$$P = x_1 p_1^* + (1 - x_1) p_2^* \quad (9)$$

At a fixed T , we can calculate the vapor pressure p_1^*, p_2^* for each component. It is then possible to determine the system pressure.

Calculation of p_1^*, p_2^* at 75°C .

$$p_1^* = \exp\left(14.2724 - \frac{2945.47}{75^{\circ}\text{C} + 224.00}\right) = 83.24\text{kPa} \quad (10)$$

$$p_2^* = \exp\left(14.2043 - \frac{2972.64}{75^\circ\text{C} + 209.00}\right) = 41.98\text{kPa} \quad (11)$$

For $x_1 = 0.6$

$$P = (0.6)(83.21\text{kPa}) + (0.4)(41.98\text{kPa}) = 66.72\text{kPa} \quad (12)$$

Find the corresponding gas phase composition y_1

$$y_1 = \frac{x_1 p_1^*}{P} = \frac{(0.6)(83.21\text{kPa})}{66.72\text{kPa}} \quad (13)$$

Repeating this calculation for various values of x_1 yields:

Table 1: Pressure composition data for acetonitrile(1)/nitrobenzene(2) at 75 C

x_1	y_1	P (kPa)
0.0	0.0	41.9827
0.1	0.18047	46.1051
0.2	0.33131	50.2275
0.3	0.45928	54.3499
0.4	0.56920	58.4723
0.5	0.66464	62.5947
0.6	0.74829	66.7171
0.7	0.82220	70.8396
0.8	0.88798	74.9620
0.9	0.94691	79.0844
1.0	1.0	83.2068

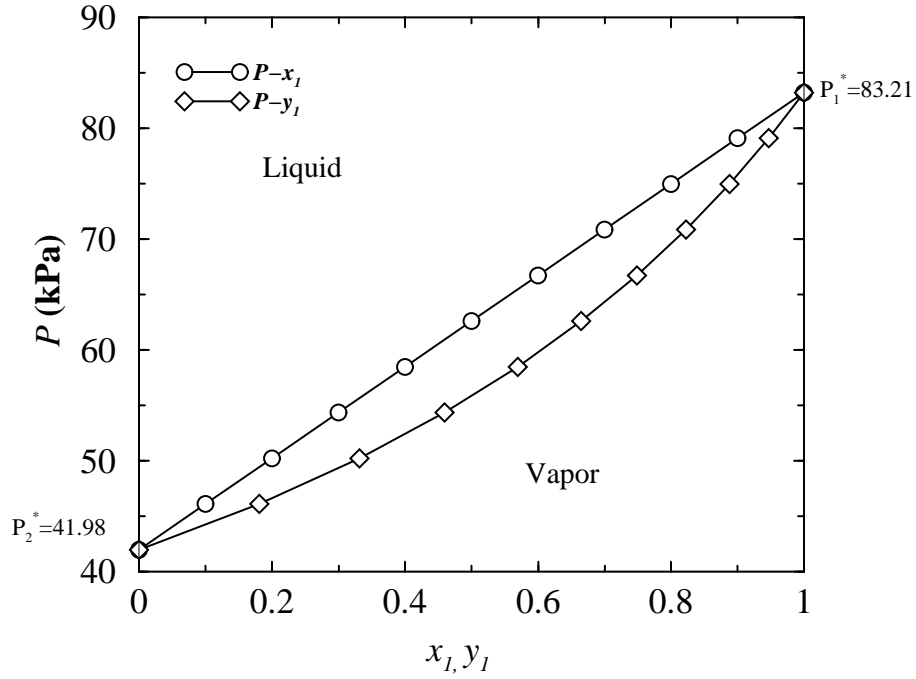


Figure 4: Pressure-composition diagram for acetonitrile(1)/nitrobenzene(2) at 75 °C. Liquid phase(circles), vapor phase(diamonds). Solid lines serve only as a guide to the eye

4.2 $T - x - y$ Calculations

In order to determine the $T - x - y$ behavior of this mixture, we need to calculate T_1^{sat} and T_2^{sat} corresponding to a pressure of 70 kPa. T^{sat} is the temperature at which the pure species exerts a vapor pressure equal to the total system pressure.

Rearrangement of equations 6 and 7 yields:

$$T_1^{\text{sat}} = \frac{-2945.47}{\ln p_1^* - 14.2724} - 224.00 = 69.84^\circ\text{C} \quad (14)$$

$$T_2^{\text{sat}} = \frac{-2972.64}{\ln p_2^* - 14.2043} - 209.00 = 89.58^\circ\text{C} \quad (15)$$

where $p_1^* = p_2^* = 70$ kPa.

All points on the phase diagram will lie between these two temperatures for a total system pressure $P = 70$ kPa. To construct the phase diagram, we vary the temperature, determine the vapor pressures, then x_1 and finally y_1 .

Rearrangement of equation 9 gives:

$$x_1 = \frac{P - p_2^*}{p_1^* - p_2^*} \quad (16)$$

For $T = 75^\circ\text{C}$, $p_1^* = 83.21 \text{ kPa}$, $p_2^* = 41.98 \text{ kPa}$. Therefore:

$$x_1 = \frac{70 - 41.98\text{kPa}}{83.21 - 41.98\text{kPa}} = 0.6796 \quad (17)$$

The gas phase composition can now be calculated from equation 13:

$$y_1 = \frac{x_1 p_1^*}{P} = \frac{(0.6796)(83.21\text{kPa})}{70\text{kPa}} = 0.808 \quad (18)$$

This process can be repeated easily with the help of a spreadsheet for the entire temperature range of interest. The results of these calculations are given in the table below:

Table 2: Temperature-composition data for acetonitrile(1)/nitrobenzene(2) at 70 kPa

x_1	y_1	T (kPa)
1.0003	1.0001	69.84
0.8596	0.9247	72.0
0.7377	0.8484	74.0
0.6232	0.7656	76.0
0.5156	0.6758	78.0
0.4141	0.5788	80.0
0.3184	0.4741	82.0
0.2279	0.3614	84.0
0.1423	0.2400	86.0
0.0612	0.1098	88.0
0.0001	0.0002	89.58

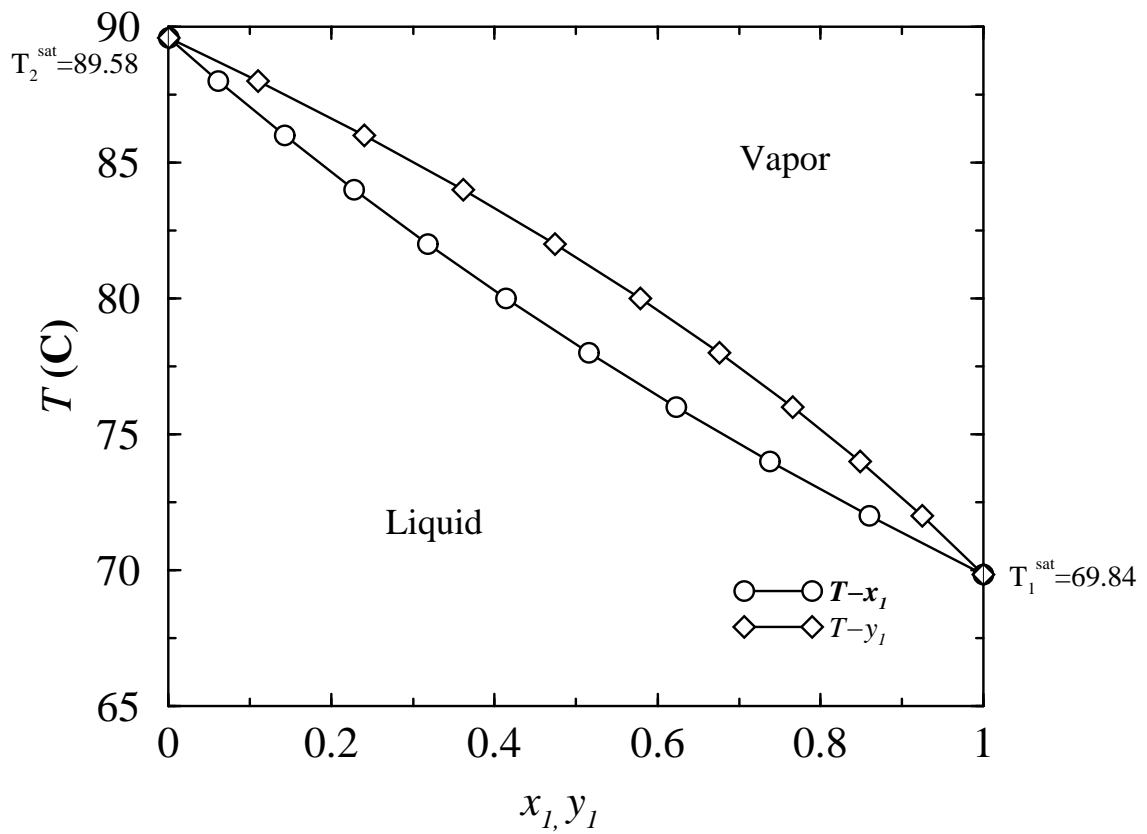


Figure 5: Temperature-composition diagram for acetonitrile(1)/nitrobenzene(2) at 70 kPa. Liquid phase(circles), vapor phase(diamonds). Solid lines serve only as a guide to the eye

5 Example #2: Bubble Temperature Calculation

Returning to the acetonitrile(1)/nitrobenzene(2) system, and specifying $x_1 = 0.6$ and $P = 70$ kPa, find the temperature of the system at equilibrium and the vapor composition.

Because the vapor pressures are dependent on temperature, this is an iterative process. Remember:

$$P = x_1 p_1^* + x_2 p_2^* \quad (19)$$

$$x_2 = 1 - x_1 \quad (20)$$

$$p_1^* = \exp\left(14.2724 - \frac{2945.47}{T + 224.00}\right) \quad (21)$$

$$p_2^* = \exp\left(14.2043 - \frac{2972.64}{T + 209.00}\right) \quad (22)$$

Upon substitution we arrive at the following expression:

$$P = x_1 \exp\left(14.2724 - \frac{2945.47}{T + 224.00}\right) + (1 - x_1) \exp\left(14.2043 - \frac{2972.64}{T + 209.00}\right) \quad (23)$$

The temperature is varied until the right hand side is equal to the system pressure of 70 kPa. This can be done manually, since convergence of these functions is generally quickly achieved, or a spreadsheet with "goal seek" functionality can be used. In this case, $T_{bt} = 76.42^\circ\text{C}$ and $y_1 = x_1 p_1^*/P = (0.6)(87.17\text{kPa})/70\text{kPa} = 0.7472$.

6 Example #3: Dew Temperature Calculation

Considering the acetonitrile(1)/nitrobenzene(2) system and given $y_1 = 0.6$ and $P = 70$ kPa, it is possible to calculate the temperature of the mixture (dew temperature) and the composition of the liquid phase. In this case, equation 4 contains the relationships we require:

$$\frac{y_1 P}{p_1^*} + \frac{y_2 P}{p_2^*} = 1 \quad (24)$$

Again, since the temperature is yet unknown, an iterative process is required due to the dependence on the vapor pressure. The resulting equation that is used for the iteration is:

$$\frac{y_1 P}{\exp\left(14.2724 - \frac{2945.47}{T + 224.00}\right)} + \frac{(1 - y_1) P}{\exp\left(14.2043 - \frac{2972.64}{T + 209.00}\right)} = 1 \quad (25)$$

After iteration, we find $T = 79.58^\circ\text{C}$ and $x_1 = \frac{(0.60)(70\text{kPa})}{96.53\text{kPa}} = 0.4351$.

7 Flash Calculations

A liquid that is at a pressure equal to or greater than its bubble pressure will partially evaporate, or “flash”, when the pressure is reduced. The result is a two phase system of vapor and liquid at equilibrium.

Consider the T,P flash. Given a temperature and pressure and an *overall* composition, we can calculate the mole fraction of each species in the liquid and vapor phases. Consider a system containing 1 mole of liquid:

- z_i = the overall composition
- L = moles of liquid, with mole fractions x_i .
- V = moles of vapor, with mole fractions y_i .
- $K_i = p^*/P = y_i/x_i$

The material balance equations are:

$$L + V = 1 \quad (26)$$

$$z_i = x_i L + y_i V \quad (27)$$

Combining 26, 27 and substituting $x_i = y_i/K_i$ yields:

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (28)$$

Since $\sum_{i=1}^n y_i = 1$, where n is the number of components:

$$\sum_{i=1}^n y_i = \frac{\sum_{i=1}^n z_i K_i}{1 + V(K_i - 1)} = 1 \quad (29)$$

Solution proceeds by iteration to find the V which satisfies this equation. **Note:** The solution $V = 1$ is always a trivial solution.

7.1 Example of a T, P Flash Calculation

A system of acetone(1)/acetonitrile(2)/nitromethane(3) at 80 °C and 110 kPa and overall compositions $z_1 = 0.45, z_2 = 0.35, z_3 = 0.20$, determine L, V, x_i, y_i . The vapor pressures of each species(in kPa) are given by:

$$p_1^* = \exp\left(14.3916 - \frac{2795.82}{T^\circ\text{C} + 230.00}\right) \quad (30)$$

$$p_2^* = \exp\left(14.2724 - \frac{2945.47}{T^\circ\text{C} + 224.00}\right) \quad (31)$$

$$p_3^* = \frac{101.325}{760} \text{ALOG}\left(7.28166 - \frac{1446.937}{T^\circ\text{C} + 227.6}\right) \quad (32)$$

7.1.1 Step 1 - Determine if we are in the two phase region

Determine bubble pressure (set $x_i = z_i$):

$$\begin{aligned} P_{bubble} &= x_1 p_1^* + x_2 p_2^* + x_3 p_3^* \\ &= (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) \\ &= 132.40\text{kPa} \end{aligned} \quad (33)$$

Determine dew pressure (set $y_i = z_i$):

$$P_{dew} = \frac{1}{\frac{y_1}{p_1^*} + \frac{y_2}{p_2^*} + \frac{y_3}{p_3^*}} = 101.52\text{kPa} \quad (34)$$

Since our pressure lies between the calculated bubble and dew pressures, we have confirmed the system is in the two-phase region. We continue our calculation by determining K_i .

$$\begin{aligned} K_1 &= \frac{p_1^*}{P} = 195.75/110 = 1.7795 \\ K_2 &= \frac{p_2^*}{P} = 97.84/110 = 0.8895 \\ K_3 &= \frac{p_3^*}{P} = 50.32/110 = 0.4575 \end{aligned} \quad (35)$$

Substitute into equation 29:

$$\frac{(0.45)(1.7795)}{1 + 0.7795V} + \frac{(0.35)(0.8895)}{1 - 0.1105V} + \frac{(0.20)(0.4575)}{1 - 5425V} = 1 \quad (36)$$

Iteration yields $V = 0.7364$ mol, $L = 0.2636$ mol. Substitution into equation 28 gives:

$$y_1 = 0.5087, \quad y_2 = 0.3389, \quad y_3 = 0.1524 \quad (37)$$

From Raoult's law:

$$x_1 = 0.2859, \quad x_2 = 0.3810, \quad x_3 = 0.3331 \quad (38)$$

References

- [1] These notes are based on the book by Smith J. M., Van Ness, H. C., and M. M. Abbott, “Introduction to Chemical Engineering Thermodynamics,” 6th ed. (McGraw-Hill) (2001).
- [2] Nist Chemistry WebBook, <http://webbook.nist.gov/chemistry/>
- [3] Reamer, H. H., B. H. Sage, and W. N. Lacey, “Phase Equilibria in Hydrocarbon Systems: Volumetric Phase Behavior of the Propane–Carbon Dioxide System,” *Ind. Eng. Chem.* **43**, 2515 (1951).
- [4] Yucelen, B., and A. J. Kidnay, “Vapor-Liquid Equilibria in the Nitrogen + Carbon Dioxide + Propane System from 240 to 330 K at Pressures to 15 MPa,” *J. Chem. Eng. Data.* **44**, 926 (1999).