

**Example 10.6:** Binary VLE Using the SRK

Use the SRK equation to calculate the  $Pxy$  graph of  $\text{CO}_2(1)/n\text{-pentane}$  at 277.65 K. The interaction parameter is  $k_{12} = 0.12$ .

**Solution** The  $Pxy$  graph is constructed by calculating a series of tie line by the method outlined above. Below we summarize the results for the tie line at  $x_1 = 0.2$ .

To initiate the calculation we need a guess for the pressure and for the mol fractions in the gas phase. For the mol fractions we use  $y_1 = x_1$ ,  $y_2 = x_2$ . For the pressure we pick  $P = 4$  bar because this pressure the SRK equation with  $T = 277.65$  K and  $x_1 = 0.2$  has three real roots. The smallest ( $Z_L = 0.0190462$ ) is used to calculate the fugacity coefficients in the liquid phase, and the largest ( $Z_V = 0.832693$ ) is used to calculate the fugacity coefficients in the vapor (which is taken to have the same composition as the vapor). The results of these calculations are shown below:

| $P = 4$ bar     | $x_i$ | $y_i$ | $\phi_i^L$ | $\phi_i^V$ | $K_i$   | $K_i x_i$ |
|-----------------|-------|-------|------------|------------|---------|-----------|
| CO <sub>2</sub> | 0.2   | 0.2   | 11.9269    | 1.06317    | 11.2183 | 2.24365   |
| n-Pentane       | 0.8   | 0.8   | 0.07461    | 0.81303    | 0.09176 | 0.07341   |
|                 | 1.0   | 1.0   |            |            |         | 2.31707   |

The new guess for the gas-phase mole fractions is

$$y_1 = \frac{K_1 x_1}{K_1 x_1 + K_2 x_2} = \frac{2.24365}{2.31707} = 0.968317,$$

$$y_2 = \frac{K_2 x_2}{K_1 x_1 + K_2 x_2} = \frac{0.07341}{2.31707} = 0.03168.$$

The calculation is then repeated with the new mole fractions (all else remains the same) until the quantity  $K_1 x_1 + K_2 x_2$  converges to a constant value. The pressure guess is then refined and the trial-end error method is repeated until the quantity  $K_1 x_1 + K_2 x_2$  converges to 1. These iterations (not shown) converge to the final result for this tie line

| $P = 10.7083$ bar | $x_i$ | $y_i$   | $\phi_i^L$ | $\phi_i^V$ | $K_i$  | $K_i x_i$ |
|-------------------|-------|---------|------------|------------|--------|-----------|
| CO <sub>2</sub>   | 0.2   | 0.96956 | 4.53038    | 0.934523   | 4.8478 | 0.96956   |
| n-Pentane         | 0.8   | 0.03044 | 0.02888    | 0.759036   | 0.0381 | 0.03044   |
|                   | 1.0   | 1.00000 |            |            |        | 1.00000   |

The bubble pressure is 10.7083 bar and the mole fraction of carbon dioxide in the vapor is  $y_1 = 0.96956$ . The complete  $Pxy$  graph is obtained by repeating the calculation at several liquid compositions between  $x_1 = 0$  and  $x_1 = 1$ , as summarized in the table below:

$T = 277.65$  K

| $P$ (bar) | $x_1$ | $y_1$  | $P$ (bar) | $x_1$ | $y_1$  |
|-----------|-------|--------|-----------|-------|--------|
| 0.29      | 0     | 0      | 27.39     | 0.6   | 0.9869 |
| 5.58      | 0.1   | 0.9444 | 30.19     | 0.7   | 0.9884 |
| 10.71     | 0.2   | 0.9696 | 32.61     | 0.8   | 0.9900 |
| 15.57     | 0.3   | 0.9781 | 35.24     | 0.9   | 0.9925 |
| 20.04     | 0.4   | 0.9824 | 39.44     | 1     | 1.0000 |
| 24.01     | 0.5   | 0.9851 |           |       |        |

The  $Pxy$  graph is shown in Figure 10-2. The data points are the experimental results of Besserer and Robinson, *Journal of Chemical and Engineering Data*, 18, no. 4 (1973). The agreement is very good. Results are also shown at 344.32 K. This temperature is above the critical temperature of  $\text{CO}_2$ , which causes the VLE region to detach from the vertical axis at  $x_1 = 1$  and to exhibit a critical point. Numerical convergence near the critical point is more difficult. For this reason, the SRK calculation at 344.32 K was conducted up to a maximum pressure of about 80 bar.

### NOTE

#### On Equations of State

The appeal of equations of state is that they can be used to obtain the entire phase behavior of a system over a wide range of pressures and temperature using tabulated values (critical properties, acentric factor) and a one adjustable parameter (interaction parameter). There are, however, two important limitations. The first one is that equations of state are generally applicable to small molecules that are chemically similar and interact via weak, nonpolar forces. While this encompasses many hydrocarbon systems that are industrially important, it excludes a much wider class of mixtures of strongly interacting molecules, including systems that contain water and other polar molecules. The second limitation is that these calculations quickly become cumbersome as the number of components increases. For this reason, alternative methods have been developed that can handle a broader variety of systems. The most widely used methodology is based on the notion of the ideal solution and makes use of activity coefficients. These topics are discussed in Chapters 11 and 12.

## 10.6 Summary

In this chapter we developed the criteria for phase equilibrium in a multicomponent mixture and showed how to construct the entire phase diagram <sup>if</sup> the equation of state is known. The most important theoretical result is equilibrium criterion which we expressed in the following equivalent forms:

$$\mu_i^L = \mu_i^V, \quad [10.6]$$

$$f_i^L = f_i^V, \quad [10.19]$$

$$x_i \phi_i^L = y_i \phi_i^V. \quad [10.20]$$

The fundamental result is eq. (10.6), which equates the chemical potentials of a component in every phase the component is present. Equations (10.19)–(10.20) express