2. Calculate the parameters a_i, b_i, of the pure components.
3. Calculate the parameters a, b, of the mixture using the mixing rules from eqs. (9.38) and (9.39).
4. Calculate the parameters A' and B' of the mixture using eq. (2.36), and the parameter C_i for each component from eq. (10.23).
5. Solve for the roots of the compressibility factor: if there are three real roots, choose based on the phase of the system.
6. Calculate the fugacity coefficients from eqs. (10.21) or (10.22) using the compressibility factor of the mixture.
7. Calculate the fugacity of each component from eq. (10.15).

This calculation is demonstrated with a numerical example below.

Example 10.5: Fugacity in Mixture Using the SRK Equation
A liquid mixture of carbon dioxide(1)/n-pentane(2) contains 32% by mole carbon dioxide. Calculate the fugacity of the two components at 4.5 °C, 16.15 bar using the SRK equation with $k_{12} = 0.12$.

Solution The critical parameters of the pure components are:

	T_c (K)	P_c (bar)	ω
CO_2 (1) :	304.2	73.74	0.225
Pentane (2) :	469.7	33.7	0.252

The various SRK parameters of the pure components and of the mixture are:

	a (J m^3/mol^2)	b (m^3/mol)	C_i (−)
CO_2	0.39863	2.97156×10^{-5}	4.75869
n-Pentane	2.78581	1.00397×10^{-4}	11.9516
Mixture	1.73256	7.77787×10^{-5}	

Using these values we find

0.0544159

$$A' = 0.525105, \quad B' = \cancel{0544159.}$$

The cubic equation for the compressibility factor is

$$Z^3 - Z^2 + 0.467728Z - 0.028574 = 0,$$

which has one real root:

$$Z = 0.0711422.$$

The fugacity coefficients of the two components are

$$\phi_1 = 2.80821, \quad \phi_2 = 0.02029.$$

Finally, the fugacity of the component in the solution is

$$f_1 = (0.32)(2.80821)(16.15) = 14.5 \text{ bar},$$
$$f_2 = (0.68)(0.02029)(16.15) = 0.223 \text{ bar}.$$

10.5 VLE of Mixture Using Equations of State

We now have all the necessary ingredients to compute the phase diagram of a mixture based entirely on an equation of state. The starting point is the equilibrium condition, which for a binary system gives

$$x_1\phi_1^L = y_1\phi_1^V, \tag{10.24}$$
$$x_2\phi_2^L = y_1\phi_2^V. \tag{10.25}$$

The variables that define a tie line are pressure, temperature, and the mole fractions in the two phases. This makes for a total of four unknowns (only one mole fraction is needed per phase as the other is calculated from the normalization condition). Given four variables and two equations, two variables must be specified in order to solve for the rest.[5] Depending on which variables are specified and which are unknown, VLE problems are classified according to the following scheme:

- *Bubble P.* Temperature and liquid-phase composition are specified; solve for bubble pressure and vapor mol fractions.
- *Bubble T.* Pressure and liquid-phase composition are specified; solve for bubble ~~pressure~~ temperature and vapor mol fractions.
- *Dew P.* Temperature and vapor-phase composition are specified; solve for dew pressure and liquid mol fractions.
- *Dew T.* Pressure and vapor-phase composition are specified; solve for dew temperature and liquid mol fractions.
- *Flash.* Pressure and temperature are specified; solve for the compositions of the two phases.

5. We obtain the same result by the phase rule: with two components ($N = 2$) and two phases ($\pi = 2$), the number of degrees of freedom is $N + 2 - \pi = 2$.