Homework 4: Problem 4.39

March 6, 2008

We are given the second virial coefficients for a mixture of n-butane (1) and carbon dioxide (2). For pressures below 15 bar, it is ok to truncate the virial expansion after the second order.

(a) Predict the molar volume of 25 mol % butane in CO_2 at 10 bar and 313.2 K.

Since the mole percent of n-butane is 25%, we know the mole fractions:

$$\begin{aligned} y_1 &= 0.25 \\ y_2 &= 0.75 \end{aligned}$$

The virial coefficients are:

$$\begin{aligned} B_{11} &= -625 \text{ [cm}^3 \text{ / mol]} \\ B_{22} &= -110 \text{ [cm}^3 \text{ / mol]} \\ B_{12} &= -153 \text{ [cm}^3 \text{ / mol]} \end{aligned}$$

From which calculate the virial coefficient for the mixture:

$$\begin{aligned} B_{mix} &= y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \\ &= -158.31 \text{ [cm}^3 \text{ / mol]} \end{aligned}$$

[+1 point]. We now substitute this value into the virial equation of state:

$$
\begin{aligned}
z &= \frac{Pv}{RT} \\
&= 1 + \frac{B_{mix}}{v}
\end{aligned}
$$

Solving the previous equation for v yields:

$$
v = \frac{1 \pm \sqrt{1 + 4PB_{mix}/RT}}{2P/RT}
$$

This equation for the specific volume has two solutions; we must determine which solution (the + or -) is the correct one. We determine this by taking the limit of v as $B_{mix} \rightarrow 0$. Since B_{mix} is a measure of the non-ideality of the mixture, as $B_{mix} \rightarrow 0$, the molar volume must limit to ideal gas behavior:

$$
\lim_{B_{mix} \rightarrow 0} v = \frac{RT}{P}
$$

Consequently, we can rule out the negative solution, $v = \frac{1-\sqrt{1+4PB_{mix}/RT}}{2P/RT}$, because it limits to zero as $B_{mix} \rightarrow 0$. The final result is:

$$
\begin{aligned}
v &= \frac{1 + \sqrt{1 + 4PB_{mix}/RT}}{2P/RT} \\
&= 2434.8 \text{ [cm}^3\text{/mol]}
\end{aligned}
$$

which is smaller than the ideal gas result of $v = 2603.1$ cm^3/mol, as one would expect. [+ 4 points, -2 if they don't explain why the -ve solution is wrong]

(b) The binary interaction parameter is not unique; it depends upon the equation of state that is chosen. You are asked to estimate the binary interaction parameter for the Redlich-Kwong EOS. Since the RK EOS and the virial EOS can be solved for the pressure, we can equate them as follows:

$$
\begin{aligned}
P_{virial} &= P_{RK} \\
\frac{RT}{v}\left(1 + \frac{B_{mix}}{v}\right) &= \frac{RT}{v - b_{mix}} - \frac{a_{mix}}{\sqrt{T}v\,(v + b_{mix})}
\end{aligned}
$$

where the a_{mix} and b_{mix} on the right-hand side are given by:

$$\begin{aligned} a_{mix} &= y_1^2 a_1 + 2 y_1 y_2 \sqrt{a_1 a_2}\,(1-k_{12}) + y_2^2 a_2 \\ b_{mix} &= y_1 b_1 + y_2 b_2 \end{aligned}$$

We can rearrange the previous equations to solve for k_{12}:

$$k_{12} = 1 + \frac{y_1^2 a_1 + y_2^2 a_2}{2 y_1 y_2 \sqrt{a_1 a_2}} - \frac{\sqrt{T}\, v\,(v + b_{mix})}{2 y_1 y_2 \sqrt{a_1 a_2}} \left[\frac{RT}{v - b_{mix}} - \frac{RT}{v} \left(1 + \frac{B_{mix}}{v} \right) \right]$$

[+1 point]. To solve for the pure-component parameters, we'll use the critical temperature and pressure for each species (from Tables A.1.1 and A.1.2):

$$\begin{aligned} T_{c,1} &= 425.2 \text{ [K]} \\ T_{c,2} &= 304.2 \text{ [K]} \\ P_{c,1} &= 37.9 \text{ [bar]} \\ P_{c,2} &= 73.76 \text{ [bar]} \end{aligned}$$

The pure component parameters for RK EOS are given by:

$$\begin{aligned} a &= 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \\ b &= 0.08664 \frac{R T_c}{P_c} \end{aligned}$$

from which it follows that:

$$\begin{aligned} a_1 &= 2.90692 \times 10^7 \text{ [J K}^{1/2}\text{ cm}^3\text{/mol}^2\text{]} \\ a_2 &= 6.46645 \times 10^6 \text{ [J K}^{1/2}\text{ cm}^3\text{/mol}^2\text{]} \\ b_1 &= 80.82 \text{ [cm}^3\text{/mol]} \\ b_2 &= 29.71 \text{ [cm}^3\text{/mol]} \end{aligned}$$

[+1 point]. plugging all these values into Matlab, we get:

$$k_{12} = 0.22264$$

[+3 points].