7.15 Consider a binary mixture of species *a* and *b* that obeys the Redlich-Kwong equation of state with van der Waals mixing rules. Show that the fugacity coefficient of species *a* in a binary mixture of *a* and *b* is given by

$$\ln(\hat{\varphi}_a) = \ln\left[\frac{RT}{Pv}\right] - \ln\left[1-\frac{b}{v}\right] + b_a\left[\frac{1}{v-b} - \frac{a}{bRT^{1.5}(v+b)}\right] + \frac{1}{bRT^{1.5}}\left[\frac{b_a a}{b} - 2\sqrt{a_a a}\right]\ln\left[1+\frac{b}{v}\right]$$

The expression for fugacity to use when a pressure-explicit EOS is given is

$$RT\ln\left[\hat{\varphi}_i\right] RT\ln\left[\frac{\hat{f}_i^v}{y_i P_{low}}\right] = -\int_{\frac{n_T RT}{P_{low}}}^{V}\left(\frac{\partial P}{\partial n_a}\right)_{T,V,n_b} dV \qquad (1)$$

We use a reference state of an ideal mixture at low pressure so that simplifications can be made at a later point.

The van der Waals mixing rules define the parameters a_{mix} and b_{mix} in the Redlich-Kwong equation of state. They are

$a_{mix}=y_a^2 a_a + 2y_b y_a a_{ab} + y_b^2 a_b$ (2)

$a_{ab}=(a_a a_b)^{1/2}$ (3)

$b_{mix}=y_a b_a + y_b b_b$ (4)

The Redlich-Kwong EOS for a mixture in terms of explicit volume V is

$$P = \frac{n_T RT}{V - n_T b_{mix}} - \frac{a_{mix} n_T{}^2}{T^{1/2} V(V + n_T b_{mix})} \qquad (5)$$

Substituting Eqs. 2-4 in Eq. 5,

$$P = \frac{(n_a + n_b)RT}{V - (n_a b_a + n_b b_b)} - \frac{n_a^2 a_a + 2n_a n_b\sqrt{a_a a_b} + n_b{}^2 a_b}{T^{1/2} V(V + (n_a b_a + n_b b_b))} \qquad (6)$$

Differentiating Eq. 6 with respect to n_a,

$$\left.\frac{\partial P}{\partial n_a}\right)_{T,V,n_b} = \frac{RT}{V - nb_{mix}} + \frac{nRTb_a}{(V - nb_{mix})^2} - \frac{2n_a a_a + 2n_b\sqrt{a_a a_b}}{T^{1/2}V(V + nb_{mix})} + \frac{b_a n^2 a_{mix}}{T^{1/2}V(V + nb_{mix})^2} \qquad (7)$$

Substituting Eq. 7 into Eq. 1 and integrating,

$$RT\ln\left[\frac{\hat{f}_a}{y_a P_{low}}\right] = -\int_{\frac{n_T RT}{P_{low}}}^{V} \left(\frac{\partial P}{\partial n_a}\right)_{T,V,n_b} dV$$

$$= -RT\ln\left[\frac{V-nb_{mix}}{\frac{nRT}{P_{low}}-nb_{mix}}\right] + \frac{nRTb_a}{V-nb_{mix}} - \frac{nRTb_a}{\frac{nRT}{P_{low}}-nb_{mix}} \tag{8}$$

$$-\frac{(2n_a a_a + 2n_b\sqrt{a_a a_b})}{\sqrt{T}nb_{mix}}\left(\ln\left[\frac{V+nb_{mix}}{\frac{nRT}{P_{low}}+nb_{mix}}\right] - \ln\left[\frac{V}{\frac{nRT}{P_{low}}}\right]\right)$$

$$+\frac{a_{mix}b_a}{\sqrt{T}b_{mix}^2}\left(\ln\left[\frac{V+nb_{mix}}{\frac{nRT}{P_{low}}+nb_{mix}}\right] - \ln\left[\frac{V}{\frac{nRT}{P_{low}}}\right]\right)$$

$$-\frac{na_{mix}b_a}{\sqrt{T}b_{mix}(V+nb_{mix})} + \frac{na_{mix}b_a}{\sqrt{T}b_{mix}\left(\frac{nRT}{P_{low}}+nb_{mix}\right)}$$

Using the approximation that b << RT/P_{low}, and dividing by RT:

$$RT\ln\left[\frac{\hat{f}_a}{y_a P_{low}}\right] = -\ln\left[\frac{V-nb_{mix}}{\frac{nRT}{P_{low}}}\right] + \frac{nb_a}{V-nb_{mix}} - \frac{nb_a}{\frac{nRT}{P_{low}}} \tag{9}$$

$$-\frac{(2n_a a_a + 2n_b\sqrt{a_a a_b})}{RT\sqrt{T}nb_{mix}}\ln\left[\frac{V+nb_{mix}}{V}\right]$$

$$+\frac{a_{mix}b_a}{RT\sqrt{T}b_{mix}^2}\ln\left[\frac{V+nb_{mix}}{V}\right]$$

$$-\frac{na_{mix}b_a}{RT\sqrt{T}b_{mix}(V+nb_{mix})} + \frac{na_{mix}b_a}{RT\sqrt{T}b_{mix}\left(\frac{nRT}{P_{low}}\right)}$$

Taking the limit as our P_{low} → 0 and adding ln P_{low} to both sides

$$\ln\left[\frac{\hat{f}_a}{y_a}\right] = -\ln\left[\frac{V-nb_{mix}}{nRT}\right] + \frac{nb_a}{V-nb_{mix}} \qquad (10)$$
$$-\frac{(2n_a a_a + 2n_b\sqrt{a_a a_b})}{RT\sqrt{T}nb_{mix}}\ln\left[\frac{V+nb_{mix}}{V}\right]$$
$$+\frac{a_{mix}b_a}{RT\sqrt{T}b_{mix}^2}\ln\left[\frac{V+nb_{mix}}{V}\right]$$
$$-\frac{na_{mix}b_a}{RT\sqrt{T}b_{mix}(V+nb_{mix})}$$

Using $\frac{V}{n} = v$ and factoring,

$$\ln\left[\frac{\hat{f}_a}{y_a}\right] = -\ln\left[\frac{v}{RT}\left(1-\frac{b_{mix}}{v}\right)\right] + \frac{b_a}{v-b_{mix}} \qquad (11)$$
$$-\left(\frac{2(y_a a_a + y_b\sqrt{a_a a_b})}{RT\sqrt{T}b_{mix}} - \frac{a_{mix}b_a}{RT\sqrt{T}b_{mix}^2}\right)\ln\left[\frac{v+b_{mix}}{v}\right]$$
$$-\frac{a_{mix}b_a}{RT\sqrt{T}b_{mix}(v+b_{mix})}$$

Now we can use the following relationship for the $(y_a a_a + y_b\sqrt{a_a a_b})$ term:

$$a_{mix} = \left(y_a\sqrt{a_a} + y_b\sqrt{a_b}\right)^2$$
$$\sqrt{a_{mix}} = y_a\sqrt{a_a} + y_b\sqrt{a_b}$$

Multiply both sides by $\sqrt{a_a}$

$$\sqrt{a_a a_{mix}} = y_a a_a + y_b\sqrt{a_a a_b} \qquad (12)$$

Replacing the $(y_a a_a + y_b\sqrt{a_a a_b})$ term with $\sqrt{a_a a_{mix}}$ and subtracting ln(P) from both sides, we get the expression found in the book:

$$\begin{aligned}\ln\left[\hat{\varphi}_a\right] &= \ln\left[\frac{\hat{f}_a}{y_a P}\right] \\ &= \ln\left[\frac{RT}{Pv}\right] - \ln\left[1-\frac{b_{mix}}{v}\right] + \frac{b_a}{v-b_{mix}} \\ &\quad -\frac{a_{mix} b_a}{RT\sqrt{T} b_{mix}(v+b_{mix})} \\ &\quad +\frac{1}{RT\sqrt{T} b_{mix}}\left(\frac{a_{mix} b_a}{b_{mix}} - 2\sqrt{a_a a_{mix}}\right)\ln\left[1+\frac{b_{mix}}{v}\right]\end{aligned} \tag{13}$$

Grading scheme:

1. 1 point for Equation 1
2. 1 point for Equation 6
3. 2 points for Equation 7
4. 2 points for Equation 8
5. 0.5 point for using the b << RT/P approximation
6. 1 point for Equation 9
7. 1 point for Equation 11
8. 1.5 points for Equation 13