CHAPTER V

THERMODYNAMIC FUNCTIONS FROM SELECTED EQUATIONS OF STATE

Derived Functions Of EOS.

Expressions for enthalpy departure, entropy departure, and component fugacity coefficient of a mixture are derived below from Equations (3-10), (3-13) and (3-17) for the five equations of state discussed in the previous sections. The thermodynamic property expressions for a pure substance are not separately derived here, because the mixture expressions also apply to pure substances.

5.1 SRK Equation Of State.

5.1.1 Enthalpy Departure.

Expressions for isothermal enthalpy departure for the Soave equations are derived from Equations (3-10) and (4-1).

$$\frac{H-H^*}{RT} = Z - 1 + \frac{1}{RT}\int_{\infty}^{V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV. \qquad (3\text{-}10)$$

Equations of state provide the P-V-T relation required to evaluate the right side of the above equation. The values of the ideal gas state enthalpy, H^*, in the left side of Equation (3-10) for pure substances, and can be calculated from Equation (3-11) for mixtures.

Differentiating Equation (4-1) with respect to T, at constant , and multiplying by T, give

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} - \frac{T}{V(V+b)}\left(\frac{da}{dT}\right). \tag{5-1}$$

The integrands in Equation (3-10) then becomes

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{1}{V(V+b)}\left[a - T\left(\frac{da}{dT}\right)\right]. \tag{5-2}$$

Combining Equation (3-10) with (5-2) and then integrating gives

$$\frac{H-H^*}{RT} = Z - 1$$

$$-\frac{1}{bRT}\left[a - T\left(\frac{da}{dT}\right)\right]\ln\left(1+\frac{b}{V}\right) \tag{5-3}$$

Making use of $(a/bRT) = (A/B)$ and $(b/V) = (B/Z)$ gives

$$\frac{H-H^*}{RT} = Z - 1$$

$$-\frac{A}{B}\left[1-\frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln\left(1+\frac{B}{Z}\right). \tag{5-4}$$

Differentiating Equation (4-7) with respect to T, at constant compositions gives

$$\frac{da}{dT}=\sum_{i}^{N}\sum_{j}^{N}x_i x_j\left[a_i^{0.5}\left(\frac{da_j^{0.5}}{dT}\right)+a_j^{0.5}\left(\frac{da_i^{0.5}}{dT}\right)\right]\left(1-k_{ij}\right) \tag{5-5}$$

$$=2\sum_{i}^{N}\sum_{j}^{N}x_i x_j a_i^{0.5}\left(\frac{da_j^{0.5}}{dT}\right)\left(1-k_{ij}\right). \tag{5-6}$$

The temperature derivative of $a_j^{0.5}$ is obtained by combining Equations (4-8) and (4-10) and (4-11) and the differentiating the resulting equation with respect to T as follows:

$$\frac{da_j^{0.5}}{dT}=\frac{d}{dT}\left\{a_{ci}^{0.5}\left[1+m_j\left(1-T_{rj}^{0.5}\right)\right]\right\}$$

$$=-\frac{1}{2T}m_j\left(a_{cj}T_{rj}\right)^{0.5}. \tag{5-7}$$

Combining Equation (5-6) and (5-7) gives

$$T\left(\frac{da}{dT}\right)=-\sum_{i}^{N}\sum_{j}^{N}x_i x_j m_j\left(a_i a_{cj}T_{rj}\right)^{0.5}\left(1-k_{ij}\right) \tag{5-8}$$

where m_j is given by Equation (4-11) and a_{cj} is given by Equation (4-9). Combining Equation (5-8) with Equations (5-3) and (5-4) separately gives

$$\frac{H-H^*}{RT}=Z-1-\frac{1}{bRT}\left[a+\sum_{i}^{N}\sum_{j}^{N}x_i x_j m_j\right.$$

$$\cdot\left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1-k_{ij}\right)\Big]\ln\left(1+\frac{b}{V}\right) \quad (5\text{-}9)$$

or

$$\frac{H-H^*}{RT}=Z-1-\frac{A}{B}\Bigg[1+\frac{1}{a}\sum_i^N\sum_j^N x_i x_j m_j$$

$$\cdot\left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1-k_{ij}\right)\Big]\ln\left(1+\frac{B}{Z}\right). \quad (5\text{-}10)$$

5.1.2 Entropy Departure.

Expressions for isothermal entropy departure are derived from Equation (3-13), which is

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln Z+\int_\infty^V\left[\frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V-\frac{1}{V}\right]dV. \quad (5\text{-}11)$$

As is the case of enthalpy departure derivations. Equation (4-1) provides the P-V-T relation required to evaluate the right side of Equation (3-13) for the Redlich-Kwong, the Wilson and the Soave equations. Thus, Equation (5-1), which is based on Equation (4-1), is also valid for the entropy departure expressions. Dividing Equation (5-1) through by RT and substracting $/V$ from both sides of the equation gives the integrand in Equation (3-13):

$$\frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V-\frac{1}{V}=\frac{b}{V(V-b)}-\frac{1}{RTV(V+b)}\left(T\frac{da}{dT}\right). \quad (5\text{-}12)$$

Combining Equation (3-13) with (5-12) and integrating the resulting equation gives

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-\frac{Pb}{RT}\right)$$

$$+\frac{1}{bRT}\left(T\frac{da}{dT}\right)\ln\left(1+\frac{b}{V}\right). \qquad (5\text{-}13)$$

Making use of $(a/bRT)=(A/B),(b/V)=(B/Z)$, and $Pb/RT=B$ gives

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln(Z-B)+\frac{A}{B}\left[\frac{T}{a}\frac{da}{dT}\right]\ln\left(1+\frac{B}{Z}\right). \qquad (5\text{-}14)$$

Combination of Equations (4-7) and (5-8) with Equations (5-13) and (5-14) gives the following Soave entropy departure expressions:

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-\frac{Pb}{RT}\right)-\frac{1}{bRT}\left[\sum_i^N\sum_j^N x_i x_j m_j\right.$$

$$\left.\cdot\left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1-k_{ij}\right)\right]\ln\left(1+\frac{b}{V}\right) \qquad (5\text{-}15)$$

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln(Z-B)-\frac{A}{B}\left[\sum_i^N\sum_j^N x_i x_j m_j\right.$$

$$\left.\cdot\left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1-k_{ij}\right)\right]\ln\left(1+\frac{B}{Z}\right). \qquad (5\text{-}16)$$

5.1.3 Fugacity Coefficient.

The fugacity coefficient expressions for the Soave equations are derived from Equations (3-17) and (4-1). Equation (3-17) is

$$\ln \phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z-1)B_i' - \frac{a}{bRT}\left(A_i' - B_i'\right)\ln\left(1 + \frac{b}{V}\right). \tag{5-17}$$

Using the notations of A and B instead of a and b gives

$$\ln \phi_i = -\ln(Z - B) + (Z-1)B_i' \quad - \frac{A}{B}\left(A_i' - B_i'\right)\ln\left(1 + \frac{B}{Z}\right) \tag{5-18}$$

where

$$A_i' = \frac{1}{an}\left[\frac{\partial(n^2 a)}{\partial n_i}\right]_{T,n_j} \tag{5-19}$$

$$B_i' = \frac{1}{b}\left(\frac{\partial(nb)}{\partial n_i}\right)_{n_j} . \tag{5-20}$$

B_i' is obtained from Equation (4-5):

$$B_i' = \frac{b_i}{b} . \tag{5-21}$$

From Equation (4-7):

$$A_i' = \frac{1}{a}\left[2a_i^{0.5}\sum_j^N x_j a_j^{0.5}\left(1 - k_{ij}\right)\right]. \tag{5-22}$$

5.2 <u>Peng-Robinson EOS.</u>

Equation (4-12) can be written as follows:

$$P = \frac{RT}{V-b} - \frac{a}{\left[V+\left(2^{0.5}+1\right)b\right]\left[V-\left(2^{0.5}-1\right)b\right]}. \tag{5-23}$$

5.2.1 Enthalpy Departure.

The integrand in Equation (3-10) is obtained from Equation (4-12), by using the same procedure used in deriving Equation (5-2):

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} - \frac{T}{\left[V+\left(2^{0.5}+1\right)b\right]\left[V-\left(2^{0.5}-1\right)b\right]}\left(\frac{da}{dT}\right) \tag{5-24}$$

where $T(da/dT)$ is given by Equation (5-8) in which m_j, a_i, and a_{cj} are represented by Equations (4-16), (4-8), and (4-15) respectively. Substracting Equation (4-12) from Equation (5-24) and combining the result equation with Equation (3-10) gives

$$\frac{H-H^*}{RT} = Z-1$$

$$+\frac{1}{RT}\left[a-T\frac{da}{dT}\right]\int_\infty^V \frac{dV}{\left[V+\left(2^{0.5}+1\right)b\right]\left[V-\left(2^{0.5}-1\right)b\right]}. \tag{5-25}$$

Integrating gives the following Peng-Robinson enthalpy departure expressions:

$$\frac{H-H^*}{RT} = Z-1 \quad -\frac{1}{2^{1.5}bRT}\left[a-T\frac{da}{dT}\right]\ln\left(\frac{V+\left(2^{0.5}+1\right)b}{V-\left(2^{0.5}-1\right)b}\right) \tag{5-26}$$

or

$$\frac{H-H^*}{RT} = Z-1-\frac{A}{2^{1.5}B}\left[1-\frac{T}{a}\frac{da}{dT}\right]\ln\left(\frac{Z+\left(2^{0.5}+1\right)B}{Z-\left(2^{0.5}-1\right)B}\right) \tag{5-27}$$

where $T\left(\frac{da}{dT}\right) = -\sum_{i}^{N}\sum_{j}^{N} x_i x_j m_j \left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1 - k_{ij}\right)$. (5-8)

5.2.2 Entropy Departure.

From Equations (5-12) and (5-7):

$$\frac{S - S_0^*}{R} + \ln\frac{P}{P_0} = \ln\left(Z - \frac{Pb}{RT}\right) + \frac{1}{2^{1.5}bRT}\left(T\frac{da}{dT}\right)\ln\left(\frac{V + \left(2^{0.5} + 1\right)b}{V - \left(2^{0.5} - 1\right)b}\right) \quad (5\text{-}28)$$

or

$$\frac{S - S_0^*}{R} + \ln\frac{P}{P_0} = \ln(Z - B) + \frac{A}{2^{1.5}B}\left[\frac{T}{a}\frac{da}{dT}\right]\ln\left(\frac{Z + \left(2^{0.5} + 1\right)B}{Z - \left(2^{0.5} - 1\right)B}\right) \quad (5\text{-}29)$$

where $T(da/dT)$ is given by Equation (5-8) in which m_j, a_i, and a_{cj} are represented by Equations (4-16), (4-8), and (4-15) respectively.

5.2.3 Fugacity Coefficient.

The fugacity coefficient expression for Peng-Robinson equation may be derived from Equations (3-17) and (4-12), by using the same procedure used for deriving Equation (5-17). The expression is

$$\ln\phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z - 1)B_i'$$

$$-\frac{a}{2^{1.5}bRT}\left(A_i' - B_i'\right)\ln\left(\frac{V + \left(2^{0.5} + 1\right)b}{V - \left(2^{0.5} - 1\right)b}\right) \quad (5\text{-}30)$$

or

$$\ln \phi_i = -\ln(Z - B) + (Z - 1)B_i'$$

$$-\frac{A}{2^{1.5}B}\left(A_i' - B_i'\right)\ln\left(\frac{Z + \left(2^{0.5} + 1\right)B}{Z - \left(2^{0.5} - 1\right)B}\right) \tag{5-31}$$

where B_i' and A_i' are given by Equations (5-21) and (5-22), but with the b_i and a_i being given by Equations (4-14) and (4-8).

5.3 ALS Equation Of State.

5.3.1 Enthalpy Departure.

Expressions for isothermal enthalpy departure for the ALS equations are derived from Equations (3-10) and (4-17). Differentiating Equation (4-17) with respect to T, at constant , and multiplying by T, give

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V - b_1} - \frac{T}{\left(V - b_2\right)\left(V + b_3\right)}\left(\frac{da}{dT}\right). \tag{5-32}$$

The integrand in Equation (3-10) then becomes

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{1}{\left(V - b_2\right)\left(V + b_3\right)}\left[a - T\left(\frac{da}{dT}\right)\right]. \tag{5-33}$$

Combining Equation (3-10) with (5-33) and then integrating gives

$$\frac{H-H^*}{RT}=Z-1$$

$$-\frac{1}{\left(b_2+b_3\right)RT}\left[a-T\left(\frac{da}{dT}\right)\right]\ln\left(\frac{V+b_3}{V-b_2}\right) \tag{5-34}$$

or

$$\frac{H-H^*}{RT}=Z-1$$

$$-\frac{A}{\left(B_2+B_3\right)RT}\left[1-\frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln\left(\frac{Z+B_3}{Z-B_2}\right) \tag{5-35}$$

where

$$B_k=\frac{Pb_k}{RT} \qquad k=1,2,3. \tag{5-36}$$

5.3.2 <u>Entropy Departure.</u>

Expressions for isothermal entropy departure are derived from Equation (3-13). Dividing Equation (5-32) through by RT and substracting $/V$ from both sides of the equation gives the integrand in Equation (3-13):

$$\frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V-\frac{1}{V}=\frac{b_1}{V\left(V-b_1\right)}-\frac{1}{RT\left(V-b_2\right)\left(V+b_3\right)}\left(T\frac{da}{dT}\right). \tag{5-37}$$

Combining Equation (3-13) with (5-37) and integrating the resulting equation gives

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-\frac{Pb_1}{RT}\right)+\frac{1}{\left(b_2+b_3\right)RT}\left(T\frac{da}{dT}\right)\ln\left(\frac{V+b_3}{V-b_2}\right) \tag{5-38}$$

or

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-B_1\right)+\frac{A}{\left(B_2+B_3\right)}\left(\frac{T}{a}\frac{da}{dT}\right)\ln\left(\frac{Z+B_3}{Z-B_2}\right). \tag{5-39}$$

5.3.3 <u>Fugacity Coefficient.</u>

The fugacity coefficient expressions for the ALS equation are derived from Equations (3-17) and (4-17).

$$\ln\phi_i=-\ln\left(Z-\frac{Pb_1}{RT}\right)+(Z-1)B'_{1i}+\frac{a}{\left(b_2+b_3\right)RT}\left(A'_i-B'_{2i}\right)\ln\left(V-b_2\right)$$

$$-\frac{a}{\left(b_2+b_3\right)RT}\left(A'_i+B'_{3i}\right)\ln\left(V+b_3\right) \tag{5-40}$$

or

$$\ln\phi_i=-\ln\left(Z-B_1\right)+(Z-1)B'_{1i}+\frac{A}{\left(B_2+B_3\right)}\left(A'_i-B'_{2i}\right)\ln\left(Z-B_2\right)$$

$$-\frac{A}{\left(B_2+B_3\right)}\left(A'_i+B'_{3i}\right)\ln\left(Z+B_3\right) \tag{5-41}$$

where

$$B'_{ki}=\frac{b_{ki}}{b_k} \qquad k=1,2,3. \tag{5-42}$$

5.4 SBC Equation Of State.

5.4.1 Enthalpy Departure.

Expressions for isothermal enthalpy departure for the SBC equations are derived from Equations (3-10) and (4-30). Differentiating Equation (4-30) with respect to T, at constant , and multiplying by T, give

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{(V-k_0\beta)} + \frac{k_0 RT}{(V-k_0\beta)^2}\left(T\frac{d\beta}{dT}\right) + \frac{k_1\beta RT}{(V-k_0\beta)^2}$$

$$+\frac{2k_0k_1\beta RT}{(V-k_0\beta)^3}\left(T\frac{d\beta}{dT}\right) + \frac{k_1 RT}{(V-k_0\beta)^2}\left(T\frac{d\beta}{dT}\right)$$

$$+\frac{1}{eV}\left(T\frac{dc}{dT}\right) - \frac{1}{(V+e)}\left[\frac{1}{e}\left(T\frac{dc}{dT}\right) - \frac{1}{(k_0\beta+e)}\left(T\frac{da}{dT}+T\frac{dc}{dT}\right)\right.$$

$$\left.+\frac{k_0(a+c)}{(k_0\beta+e)^2}\left(T\frac{d\beta}{dT}\right)\right] - \frac{1}{(V-k_0\beta)}\left[\frac{1}{(k_0\beta+e)}\left(T\frac{da}{dT}+T\frac{dc}{dT}\right)\right.$$

$$\left.-\frac{k_0(a+c)}{(k_0\beta+e)^2}\left(T\frac{d\beta}{dT}\right)\right] - \frac{k_0(a+c)}{(k_0\beta+e)(V-k_0\beta)^2}\left(T\frac{d\beta}{dT}\right). \qquad (5\text{-}43)$$

The integrand in Equation (3-10) then becomes

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{(V-k_0\beta)^2}\left[T\left(\frac{d\beta}{dT}\right)\right]\left(k_0 + k_1 + \frac{2k_0k_1\beta}{(V-k_0\beta)}\right)$$

$$-\frac{1}{e}\left[\frac{1}{V}-\frac{1}{(V+e)}\right]\left[c-T\left(\frac{dc}{dT}\right)\right]$$

$$-\frac{1}{\left(k_0\beta+e\right)}\left[\frac{1}{(V+e)}-\frac{1}{\left(V-k_0\beta\right)}\right]\left\{\left[a-T\frac{da}{dT}\right]+\left[c-T\frac{dc}{dT}\right]\right\}$$

$$-\frac{k_0(a+c)}{\left(k_0\beta+e\right)^2}\left(T\frac{d\beta}{dT}\right)\left\{\frac{1}{(V+e)}\right.$$

$$\left.-\frac{1}{\left(V-k_0\beta\right)}+\frac{\left(k_0\beta+e\right)}{\left(V-k_0\beta\right)^2}\right\}. \qquad (5\text{-}44)$$

Combining Equation (3-10) with (5-44) and then integrating gives

$$\frac{H-H^*}{RT}=Z-1-\frac{\left(k_0+k_1\right)}{\left(V-k_0\beta\right)}\left(T\frac{d\beta}{dT}\right)-\frac{k_0k_1\beta}{\left(V-k_0\beta\right)^2}\left(T\frac{dB}{dT}\right)$$

$$-\frac{1}{\left(k_0\beta+e\right)RT}\left\{\left[a-T\left(\frac{da}{dT}\right)\right]+\left[c-T\left(\frac{dc}{dT}\right)\right]\right\}\ln\left(\frac{V+e}{V-k_0\beta}\right)$$

$$+\frac{1}{eRT}\left[c-T\left(\frac{dc}{dT}\right)\right]\ln\left(1+\frac{e}{V}\right)$$

$$-\frac{k_0(a+c)}{\left(k_0\beta+e\right)^2RT}\left(T\frac{d\beta}{dT}\right)\left\{\ln\frac{(V+e)}{\left(V-k_0\beta\right)}-\frac{\left(k_0\beta+e\right)}{\left(V-k_0\beta\right)}\right\}. \qquad (5\text{-}45)$$

Same procedure as Equation (5-8) gives

for $T_r <= 1$,

$$T\left(\frac{da}{dT}\right)=a_c\sqrt{\alpha}\left(-\sqrt{T_r}\right)\left(X_2+2X_3\left(1-\sqrt{T_r}\right)+3X_4\left(1-\sqrt{T_r}\right)^2\right) \qquad (5\text{-}46)$$

and for $T_r > 1$,

$$T\left(\frac{da}{dT}\right) = a_c\sqrt{\alpha}\left(-\sqrt{T_r}\right)\left(X_2 + 2X_5\left(1-\sqrt{T_r}\right) + 3X_6\left(1-\sqrt{T_r}\right)^2\right) \tag{5-47}$$

and

$$T\left(\frac{d\beta}{dT}\right) = 3\beta\left[-0.03125 - 2 * 0.0054\ln\left(T_r\right)\right] \tag{5-48}$$

and finally,

$$T\left(\frac{dc}{dT}\right) = c_c\sqrt{\xi}\left(-\sqrt{T_r}\right)X_7. \tag{5-49}$$

5.4.2 Entropy Departure.

Expressions for isothermal entropy departure are derived from Equation (3-13). Dividing Equation (5-43) through by RT and substracting $/V$ from both sides of the equation gives the integrand in Equation (3-13):

$$\frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{V} = \frac{k_0\beta}{V\left(V-k_0\beta\right)} + \frac{k_1\beta}{\left(V-k_0\beta\right)^2}$$
$$+\frac{\left(k_0+k_1\right)}{\left(V-k_0\beta\right)^2}\left(T\frac{d\beta}{dT}\right) + \frac{2k_0k_1\beta}{\left(V-k_0\beta\right)^3}\left(T\frac{d\beta}{dT}\right)$$

$$+\frac{1}{e}\left[\frac{1}{V} - \frac{1}{(V+e)}\right]\left[T\left(\frac{dc}{dT}\right)\right]$$

$$-\frac{1}{(k_0\beta+e)}\left[\frac{1}{(V+e)}-\frac{1}{(V-k_0\beta)}\right]\left\{-\left[T\frac{da}{dT}+T\frac{dc}{dT}\right]\right\}$$

$$-\frac{k_0(a+c)}{(k_0\beta+e)^2}\left(T\frac{d\beta}{dT}\right)\left\{\frac{1}{(V+e)}\right.$$

$$\left.-\frac{1}{(V-k_0\beta)}+\frac{(k_0\beta+e)}{(V-k_0\beta)^2}\right\}. \qquad (5\text{-}50)$$

Combining Equation (3-13) with (5-50) and integrating the resulting equation gives

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-\frac{Pk_0\beta}{RT}\right)-\frac{k_1\beta}{(V-k_0\beta)}$$

$$-\frac{(k_0+k_1)}{(V-k_0\beta)}\left(T\frac{d\beta}{dT}\right)-\frac{k_0k_1\beta}{(V-k_0\beta)^2}\left(T\frac{d\beta}{dT}\right)$$

$$+\frac{1}{(k_0\beta+e)RT}\left\{T\left(\frac{da}{dT}\right)+T\left(\frac{dc}{dT}\right)\right\}\ln\left(\frac{V+e}{V-k_0\beta}\right)$$

$$-\frac{1}{eRT}\left[T\left(\frac{dc}{dT}\right)\right]\ln\left(1+\frac{e}{V}\right)$$

$$-\frac{k_0(a+c)}{(k_0\beta+e)^2RT}\left(T\frac{d\beta}{dT}\right)\left\{\ln\frac{(V+e)}{(V-k_0\beta)}-\frac{(k_0\beta+e)}{(V-k_0\beta)}\right\}. \qquad (5\text{-}51)$$

5.4.3 Fugacity Coefficient.

The fugacity coefficient expressions for the SBC equation are derived from Equations (3-17) and (4-30).

$$\ln\phi_i = -\ln\left(Z - \frac{Pk_0\beta}{RT}\right) + \frac{(k_0 + k_1)\beta}{(V - k_0\beta)} + \frac{k_0k_1\beta^2}{(V - k_0\beta)^2}$$

$$+ \frac{c}{RT(V+e)} + \frac{c}{eRT}\ln\left(1 + \frac{e}{V}\right)$$

$$- \frac{(a+c)}{(k_0\beta + e)RT}\left[\frac{e}{(V+e)} + \frac{k_0\beta}{(V - k_0\beta)}\right]$$

$$- \frac{(a+c)}{(k_0\beta + e)RT}\ln\frac{(V+e)}{(V - k_0\beta)}. \quad (5\text{-}52)$$

5.5 TCC Equation Of State.

5.5.1 Enthalpy Departure.

Expressions for isothermal enthalpy departure for the TCC equation are derived from Equations (3-10) and (4-68). Differentiating Equation (4-68) with respect to T, at constant , and multiplying by T, give

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} - \frac{2}{(2V + 4b + c + w)(2V + 4b + c - w)}\left(T\frac{da}{dT}\right). \quad (5\text{-}53)$$

The integrand in Equation (3-10) then becomes

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{2}{(2V + 4b + c + w)(2V + 4b + c - w)}\left[a - T\left(\frac{da}{dT}\right)\right]. \quad (5\text{-}54)$$

Combining Equation (3-10) with (5-54) and then integrating gives

$$\frac{H-H^*}{RT}=Z-1$$

$$-\frac{1}{wRT}\left[a-T\left(\frac{da}{dT}\right)\right]\ln\left(\frac{2V+4b+c+w}{2V+4b+c-w}\right) \qquad (5\text{-}55)$$

or

$$\frac{H-H^*}{RT}=Z-1-\frac{A}{W}\left[1-\frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln(\Phi) \qquad (5\text{-}56)$$

where

$$=\left(16B^2+4BC+C^2\right)^{1/2} \qquad (5\text{-}57)$$

$$\Phi=\frac{2Z+4B+C+W}{2Z+4B+C-W}. \qquad (5\text{-}58)$$

5.6.2 Entropy Departure.

Expressions for isothermal entropy departure are derived from Equation (3-13). Dividing Equation(5-53) through by RT and substracting $/V$ from both sides of the equation gives the integrand in Equation (3-13):

$$\frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V-\frac{1}{V}=\frac{b}{V(V-b)}$$

$$-\frac{2}{RT(2V+4b+c+w)(2V+4b+c-w)}\left(T\frac{da}{dT}\right). \qquad (5\text{-}59)$$

Combining Equation (3-13) with (5-59) and integrating the resulting equation gives

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln\left(Z-\frac{Pb}{RT}\right)$$

$$+\frac{2}{wRT}\left(T\frac{da}{dT}\right)\ln\left(\frac{2V+4b+c+w}{2V+4b+c-w}\right) \tag{5-60}$$

or

$$\frac{S-S_0^*}{R}+\ln\frac{P}{P_0}=\ln(Z-B)+\frac{A}{W}\left(\frac{T}{a}\frac{da}{dT}\right)\ln(\Phi). \tag{5-61}$$

5.6.3 Fugacity Coefficient.

The fugacity coefficient expressions for the TCC equation of state are derived from Equations (3-17) and (4-68).

$$\ln\phi_i=\frac{B_i}{Z-B}-\ln(Z-B)+\frac{A}{W}\left\{\Theta_i-\frac{1}{a}\left[\sum_j x_j\left(a_{ij}^0+a_{ji}^0\right)+\in_i\right]\right\}\ln(\Phi)$$

$$+\left(\frac{1}{Z-B}-1\right)\left\{\frac{1}{2}\left(4B_i+C_i\right)-\Theta_i\left[Z+\frac{1}{2}(4B+C)\right]\right\} \tag{5-62}$$

where

$$a_{ij}^0=\left(a_i a_j\right)^{1/2}\left(1-\frac{k_{ij}}{T}\right) \tag{5-63}$$

$$\Theta_i=\frac{1}{W^2}\left[2(8B+C)B_i+(2B+C)C_i\right]. \tag{5-64}$$

$\in_i$ is due to the composition-dependent term in the mixing rule,

$$\in_i = \frac{\left[\sum_j H_{ij}^{1/3} G_{ij}^{1/3} \left(a_i a_j\right)^{1/6} x_j\right]^3}{\sum_j G_{ij} x_j}$$

$$+3\sum_j x_j \frac{\left[\sum_k H_{jk}^{1/3} G_{jk}^{1/3} \left(a_j a_k\right)^{1/6} x_k\right]^2 \left[H_{ji}^{1/3} G_{ji}^{1/3} \left(a_j a_i\right)^{1/6}\right]}{\sum_k G_{jk} x_k}$$

$$-\sum_j x_j \frac{\left[\sum_k H_{jk}^{1/3} G_{jk}^{1/3} \left(a_j a_k\right)^{1/6} x_k\right]^3}{\sum_k G_{jk} x_k} \left[1 + \frac{G_{ji}}{\sum_k G_{jk} x_k}\right]. \qquad (5\text{-}65)$$