**Appendix A: Thermodynamic Properties of the Ideal-Gas**

The molar enthalpy, entropy and Helmholtz free energy of a pure ideal-gas can be expressed according to:

\[
H^o(T) = U^o_0 + (\gamma_0 + R)(T - T_0) + \frac{1}{2} \gamma_1 (T^2 - T_0^2) + \frac{1}{3} \gamma_2 (T^3 - T_0^3) + \frac{1}{4} \gamma_3 (T^4 - T_0^4) \tag{A.1}
\]

\[
S^o(T, \rho^o) = S^o_0 + \rho_0 \ln \left( \frac{T}{T_0} \right) + \gamma_1 (T - T_0) + \frac{1}{2} \gamma_2 (T^2 - T_0^2) + \frac{1}{3} \gamma_3 (T^3 - T_0^3) + R \ln \left( \frac{\rho_0}{\rho^o} \right) \tag{A.2}
\]

\[
A^o(T, \rho^o) = U^o_0 - T S^o_0 + \rho_0 T \left[ 1 - \frac{T_0}{T} \ln \left( \frac{T_0}{T} \right) \right] - \frac{1}{2} \gamma_1 T^2 \left[ 1 - \frac{T_0}{T} \right]^2 - \frac{1}{6} \gamma_2 T^3 \left[ 1 + 2 \left( \frac{T_0}{T} \right)^3 - 3 \left( \frac{T_0}{T} \right)^2 \right] - \frac{1}{12} \gamma_3 T^4 \left[ 1 + 3 \left( \frac{T_0}{T} \right)^3 - 3 \left( \frac{T_0}{T} \right)^4 \right] + RT \ln \left( \frac{\rho^o}{\rho_0} \right) \tag{A.3}
\]

For an ideal-gas binary mixture, the molar enthalpy, entropy and Helmholtz free energy can be derived from Eqs. (A.1)-(A.3) using the following relations:

\[
H^o(T, x) = x H^o_1(T) + (1 - x) H^o_2(T) \tag{A.4}
\]

\[
S^o(T, \rho^o, x) = x S^o_1(T, \rho^o) + (1 - x) S^o_2(T, \rho^o) - R \left[ x \ln x + (1 - x) \ln (1 - x) \right] \tag{A.4}
\]

\[
A^o(T, \rho^o, x) = x A^o_1(T, \rho^o) + (1 - x) A^o_2(T, \rho^o) + RT \left[ x \ln x + (1 - x) \ln (1 - x) \right] \tag{A.5}
\]

**Appendix B: Thermodynamic Properties with GEOS Model**

The vapor-liquid phase behavior of a binary system is calculated by the simultaneous salvation of the following equalities:

\[
P = P(T, \rho_L, x) \tag{B.1}
\]

\[
P = P(T, \rho_v, y) \tag{B.2}
\]

\[
x \phi_1(T, \rho_L, x) = y \phi_1(T, \rho_v, y) \tag{B.3}
\]

\[
(1 - x) \phi_2(T, \rho_L, x) = (1 - y) \phi_2(T, \rho_v, y) \tag{B.4}
\]

\(\phi\) represents the fugacity coefficient of compound i; x and y the liquid and vapor mole compositions of compound 1.

The Compressibility factor is written as:

\[
Z = \frac{1}{1 - b \rho} - \frac{a \rho^2}{RT (1 - d \rho)^2 + c \rho^2} \tag{B.5}
\]

The fugacity coefficient of compound i:

\[
\ln \phi_i = - \ln \left( 1 - b \rho \right) + \frac{b \rho \phi}{1 - b \rho} + \frac{a}{4RT \delta} \left( \frac{c}{e} - 2 \frac{a}{a_n} \right) \ln \left( \frac{1 - \partial_i \rho}{1 - \partial_n \rho} \right) - \frac{d_n \rho + c_n (1 - d \rho)}{2c} \left( \frac{a \rho}{RT (1 - d \rho)^2 + c \rho^2} \right) \ln Z \tag{B.6}
\]

\[
a^{\text{res}} = - \ln \left( 1 - b \rho \right) + \frac{a}{2RT \delta} \ln \left( \frac{1 - \partial \rho}{1 - \partial_n \rho} \right) - \ln Z \tag{B.7}
\]

\[
h^{\text{res}} = \frac{T \alpha_i}{2RT \delta} \left[ \frac{1 - \partial_i \rho}{1 - \partial_n \rho} \right] + (Z - 1) \tag{B.8}
\]

The reduced residual molar entropy:
\[ s^{res} = \ln \left( 1 - b \rho \right) + \frac{a_T}{2R\delta} \ln \left| \frac{1 - \delta_1 \rho}{1 - \delta_2 \rho} \right| + \ln Z \]  
(B.9)

The coefficients \( a, b, c \) and \( d \) are evaluated with Eqs. (32)-(36). The derivative according to \( T \) of the coefficient \( a \) can be calculated as follows:

\[ a'_T = \left( \frac{\partial a}{\partial T} \right)_{\rho,n} = \sum_{i,j} x_i x_j \left( \frac{\partial a_{ij}}{\partial T} \right)_{\rho,n} \]  
(B.10)

\[ \left( \frac{\partial a_{ij}}{\partial T} \right)_{\rho,n} = \frac{1 - k_{ij} + x_i \left( k_{ij} - k_{ji} \right)}{2a_i a_j} \left[ \frac{\partial a_i}{\partial T} \right]_{\rho,n} + \frac{a_j}{a_i} \left( \frac{\partial a_j}{\partial T} \right)_{\rho,n} \]  
(B.11)

\[ \left( \frac{\partial a_i}{\partial T} \right)_{\rho,n} = \Omega_{n_i} \frac{R^2 T_{c_i}^2}{P_{c_i}} 2a \left( T_r \right) \left( \frac{da_i}{dT} \right) \]  
(B.12)

\[ \left( \frac{da_i}{dT} \right) = \gamma_{1,i} \gamma_{2,i} + \gamma_{2,i} \left( \gamma_{1,i} \right)^2 + \gamma_{3,i} \left( \gamma_{1,i} \right)^3 ; \text{ for } T_r \leq 1 \]  
(B.13)

\[ \left( \frac{da_i}{dT} \right) = \gamma_{1,i} \gamma_{2,i} ; \text{ for } T_r > 1 \]  
(B.14)

\[ \gamma_{1,i} = \left( \frac{dy_i}{dT} \right) = -\frac{1}{2} \frac{1}{\sqrt{T_{c_i} T}} \]  
(B.15)

The derivatives according to the mole fraction \( n_{-1} \) and \( n_{-2} \) of the coefficients \( a, b, c \) and \( d \) are:

\[ a'_{n_1} = \left( \frac{\partial a}{\partial n_1} \right)_{T,\rho,n_2} = 2x_i a_{11} + x_2 \left( a_{12} + a_{21} \right) + 2x_1 x_2 \left( k_{12} - k_{21} \right) \sqrt{a_1 a_2} \]  
(B.16)

\[ a'_{n_2} = \left( \frac{\partial a}{\partial n_2} \right)_{T,\rho,n_1} = 2x_i a_{22} + x_1 \left( a_{12} + a_{21} \right) + 2x_2 x_1 \left( k_{21} - k_{12} \right) \sqrt{a_1 a_2} \]  
(B.17)

\[ b'_{n_1} = \left( \frac{\partial b}{\partial n_1} \right)_{T,\rho,n_2} = 2 \left( x_i b_{11} + x_2 b_{12} \right) - b \]  
(B.18)

\[ b'_{n_2} = \left( \frac{\partial b}{\partial n_2} \right)_{T,\rho,n_1} = 2 \left( x_i b_{21} + x_2 b_{22} \right) - b \]  
(B.19)

\[ c'_{n_1} = \left( \frac{\partial c}{\partial n_1} \right)_{T,\rho,n_2} = 2 \left( x_i c_{11} + x_2 c_{12} \right) \]  
(B.20)

\[ c'_{n_2} = \left( \frac{\partial c}{\partial n_2} \right)_{T,\rho,n_1} = 2 \left( x_2 c_{22} + x_1 c_{12} \right) \]  
(B.21)

\[ d'_{n_1} = \left( \frac{\partial d}{\partial n_1} \right)_{T,\rho,n_2} = d_1 \]  
(B.22)

\[ d'_{n_2} = \left( \frac{\partial d}{\partial n_2} \right)_{T,\rho,n_1} = d_2 \]  
(B.23)

The quantities \( \delta_{11} \) and \( \delta_{12} \) are calculated according to:

\[ \delta = \sqrt{\delta_1^2 + \delta_2^2} \]  
(B.24)