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:

$$H^{o}\left(T\right)=U_0^{o}+\left(\gamma_0+R\right)\left(T-T_0\right)+\frac{1}{2}\gamma_1\left(T^2-T_0^2\right)+\frac{1}{3}\gamma_2\left(T^3-T_0^3\right)+\frac{1}{4}\gamma_3\left(T^4-T_0^4\right) \quad \text{(A.1)}$$

$$S^{o}\left(T,\rho^{o}\right)=S_0^{o}+\gamma_0\ \ln\left(\frac{T}{T_0}\right)+\gamma_1\left(T-T_0\right)+\frac{1}{2}\gamma_2\left(T^2-T_0^2\right)+\frac{1}{3}\gamma_3\left(T^3-T_0^3\right)+R\ln\left(\frac{\rho_0}{\rho^{o}}\right) \quad \text{(A.2)}$$

$$A^{o}\left(T,\rho^{o}\right)=U_0^{o}-TS_0^{o}+\gamma_0 T\left[1-\frac{T_0}{T}+\ln\left(\frac{T_0}{T}\right)\right]-\frac{1}{2}\gamma_1 T^2\left[1-\frac{T_0}{T}\right]^2-\frac{1}{6}\gamma_2 T^3\left[1+2\left(\frac{T_0}{T}\right)^3-3\left(\frac{T_0}{T}\right)^2\right]$$
$$-\frac{1}{12}\gamma_3 T^4\left[1+3\left(\frac{T_0}{T}\right)4-3\left(\frac{T_0}{T}\right)^3\right]+RT\ \ln\left(\frac{\rho^{o}}{\rho_o}\right) \quad \text{(A.3)}$$

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:

$$H^{o}\left(T,x\right)=xH_1^{o}\left(T\right)+\left(1-x\right)H_2^{o}\left(T\right) \quad \text{(A.4)}$$

$$S^{o}\left(T,\rho^{o},x\right)=xS_1\left(T,\rho^{o}\right)+\left(1-x\right)S_2^{o}\left(T,\rho^{o}\right)-R\left[x\ln x+\left(1-x\right)\ln\left(1-x\right)\right] \quad \text{(A.4)}$$

$$A^{o}\left(T,\rho^{o},x\right)=xA_1^{o}\left(T,\rho^{o}\right)+\left(1-x\right)A_2^{o}\left(T,\rho^{o}\right)+RT\left[x\ln x+\left(1-x\right)\ln\left(1-x\right)\right] \quad \text{(A.5)}$$

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:

$$P=P\left(T,\rho_L,x\right) \quad \text{(B.1)}$$

$$P=P\left(T,\rho_V,y\right) \quad \text{(B.2)}$$

$$x\varphi_1\left(T,\rho_L,x\right)=y\varphi_1\left(T,\rho_V,y\right) \quad \text{(B.3)}$$

$$\left(1-x\right)\varphi_2\left(T,\rho_L,x\right)=\left(1-y\right)\varphi_2\left(T,\rho_V,y\right) \quad \text{(B.4)}$$

φ_i 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:

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

The fugacity coefficient of compound i:

$$\ln\varphi_i=-\ln\left(1-b\rho\right)+\frac{b'_{n_i}\rho}{1-b\rho}+\frac{a}{4RT\delta}\left(\frac{c'_{n_i}}{c}-2\frac{a'_{n_i}}{a}\right)\ln\left|\frac{1-\vartheta_1\rho}{1-\vartheta_2\rho}\right|-\left[d'_{n_i}\rho+\frac{c'_{n_i}\left(1-d\rho\right)}{2c}\right]\frac{a\rho}{RT\left[\left(1-d\rho\right)^2+c\rho^2\right]}-\ln \mathrm{Z} \quad \text{(B.6)}$$

$$a^{res}=-\ln\left(1-b\rho\right)+\frac{a}{2RT\delta}\ln\left|\frac{1-\vartheta_1\rho}{1-\vartheta_2\rho}\right|-\ln \mathrm{Z} \quad \text{(B.7)}$$

$$h^{res}=\frac{Ta'_T-a}{2RT\delta}\ln\left|\frac{1-\vartheta_1\rho}{1-\vartheta_2\rho}\right|+\left(Z-1\right) \quad \text{(B.8)}$$

The reduced residual molar entropy:

$$s^{res} = \ln\left(1 - b\rho\right) + \frac{a_T^{'}}{2R\delta}\ln\left|\frac{1-\vartheta_1\rho}{1-\vartheta_2\rho}\right| + \ln Z \qquad \text{(B.9)}$$

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:

$$a_T^{'} = \left(\frac{\partial a}{\partial T}\right)_{\rho,n} = \sum_i\sum_j x_i x_j \left(\frac{\partial a_{ij}}{\partial T}\right)_{\rho,n} \qquad \text{(B.10)}$$

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

$$\left(\frac{\partial a_i}{\partial T}\right)_{\rho,n_k} = \Omega_{a_i}\frac{R^2 T_{C_i}^2}{P_{C_i}} 2\alpha\left(T_r\right)\left(\frac{d\alpha_i}{dT}\right) \qquad \text{(B.12)}$$

$$\left(\frac{d\alpha_i}{dT}\right) = \gamma_{1,i} y_{i,T}^{'} + \gamma_{2,i}\left(y_{i,T}^{'}\right)^2 + \gamma_{3,i}\left(y_{i,T}^{'}\right)^3 \;; \quad \text{for } T_r \le 1 \qquad \text{(B.13)}$$

$$\left(\frac{d\alpha_i}{dT}\right) = \gamma_{1,i} y_{i,T}^{'} \;; \quad \text{for } T_r > 1 \qquad \text{(B.14)}$$

$$y_{i,T}^{'} = \left(\frac{dy_i}{dT}\right) = -\frac{1}{2\sqrt{T_{C_i} T}} \qquad \text{(B.15)}$$

The derivatives according to the mole fraction n_1 and n_2 of the coefficients a, b, c and d are:

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

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

$$b_{n_1}^{'} = \left(\frac{\partial b}{\partial n_1}\right)_{T,\rho,n_2} = 2\left(x_1 b_{11} + x_2 b_{12}\right) - b \qquad \text{(B.18)}$$

$$b_{n2}^{'} = \left(\frac{\partial b}{\partial n2}\right)_{T,\rho,n_1} = 2\left(x_1 b_{11} + x_2 b_{12}\right) - b \qquad \text{(B.19)}$$

$$c_{n_1}^{'} = \left(\frac{\partial c}{\partial n_1}\right)_{T,\rho,n_2} = 2\left(x_1 c_{11} + x_2 c_{12}\right) \qquad \text{(B.20)}$$

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

$$d_{n_1}^{'} = \left(\frac{\partial d}{\partial n_1}\right)_{T,\rho,n_2} = d_1 \qquad \text{(B.22)}$$

$$d_{n2}^{'} = \left(\frac{\partial d}{\partial n2}\right)_{T,\rho,n_2} = d_2 \qquad \text{(B.23)}$$

The quantities δ, ϑ_1 and ϑ_2 are calculated according to:

$$\delta = \sqrt{|c|} \quad \vartheta_1 = d - \delta \quad \vartheta_2 = d + \delta \qquad \text{(B.24)}$$