CHAPTER V

THERMODYNAMIC PROPERTIES BY SRK EQUATION

5.1 Soave-Redlich-Kwong Equation

The Soave-Redlich-Kwong equation of state may be written in the following general from:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{5-1}$$

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z - AB = 0 \tag{5-2}$$

where

$$A = \frac{aP}{(RT)^2} \tag{5-3}$$

$$B = \frac{bP}{RT} \tag{5-4}$$

Mixing Rules

The equations of state are generally developed for pure fluids first, then extended to mixtures. The mixture extension requires so-called mixing rules, which are simply means of calculating mixture parameters equivalent to those of pure substance. Except for those of virile coefficients, the mixing rules are more or less arbitrary rules that are to reflect the composition effect on the system properties.

All the pure fluid parameter symbols should have had subscript "i" which was omitted for simplicity. The subscript i will be retained to distinguish the pure fluid parameters from its mixture counterparts. Then, the mixing rule for b and a are

$$b = \sum^{N} x_i b_i \qquad (5\text{-}5)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_c} \qquad (5\text{-}6)$$

$$a = \sum_{i}^{N} \sum_{j}^{N} x_i x_j \left(a_i a_j\right)^{0.5} \left(1 - k_{ij}\right) \qquad (5\text{-}7)$$

$$a_i = a_{ci} \alpha_i \qquad (5\text{-}8)$$

$$a_{ci} = 0.42748 \frac{\left(RT_{ci}\right)^2}{P_{ci}} \qquad (5\text{-}9)$$

$$\alpha_i^{0.5} = 1 + m_i \left(1 - T_{ri}^{0.5}\right) \qquad (5\text{-}10)$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \qquad (5\text{-}11)$$

5.2 Enthalpy Departure by SRK Equation

Expression for enthalpy departure of a mixture is as follow:

$$\frac{H - H^*}{RT} = Z - 1 + \frac{1}{RT} \int_{\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \qquad (5\text{-}12)$$

Expression for isothermal enthalpy departure based on the SRK equation can be derived as follows. 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 (5-12) are given for pure substances, and can be calculated for Equation $H^* = \sum_i^N x_i H_i^*$ for mixtures.

Differentiating Equation (5-1) with respect to T, at constant V, and multiplying by T, give

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{R-T}{V-b} - \frac{T}{V(V+b)}\left(\frac{da}{dT}\right) \tag{5-13}$$

The integrand in Equation (5-12) then becomes

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{1}{V(V+b)}\left[a - T\left(\frac{da}{dT}\right)\right] \tag{5-14}$$

Combining Equation (5-12) with (5-14) and then integrating gives

$$\frac{H-H^*}{RT} = Z - 1 - \frac{1}{bRT}\left[a - T\left(\frac{da}{dT}\right)\right]\ln\left(1+\frac{b}{V}\right) \tag{5-15}$$

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

$$\frac{H-H^*}{RT} = Z - 1 - \frac{A}{B}\left[1 - \frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln\left(1+\frac{B}{Z}\right) \tag{5-16}$$

where

$$T\left(\frac{da}{dT}\right) = -\sum_i^N \sum_j^N x_i x_j m_j \left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1-k_{ij}\right) \tag{5-17}$$

5.3 Fugacity Coefficient by SRK Equation

Expressions for component fugacity coefficient of a mixture are derived below from Equations (5-18) and (5-1). Equation (5-18) is

$$\ln \Phi_i = \frac{1}{RT}\int_{\infty}^{V_t}\left[\frac{RT}{V_t} - \left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j}\right] dV_t - \ln Z \tag{5-18}$$

The derivative in this equation can be obtained from Equation (5-1) written in terms of total volume, $_t$.

$$P = \frac{nRT}{V_t - nb} - \frac{n^2 a}{V_t(V_t + nb)} \tag{5-19}$$

Differentiating P in this equation with respect to n_i, at constant T, $_t$ and n_j, gives

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j} = \frac{RT}{V_t - nb} - \left[\frac{nRT}{(V_t - nb)^2} + \frac{n^2 a}{V_t(V_t + nb)}\right]\left(\frac{\partial\ (nb)}{\partial n_i}\right)_{n_j}$$
$$+ \frac{1}{V_t(V_t + nb)}\frac{\partial}{\partial n_i}(n^2 a)_{T,n_j} \tag{5-20}$$

Combining Equation (5-18) and (5-20) and making the integration give

$$\ln \Phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z-1)B_i' - \frac{a}{bRT}(A_i' - B_i')\ln\left(1 + \frac{b}{V}\right) \tag{5-21}$$

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

$$\ln\Phi_i = -\ln(Z-B)+(Z-1)B_i' - \frac{A}{B}\left(A_i' - B_i'\right)\ln\left(1+\frac{B}{Z}\right) \qquad (5\text{-}22)$$

where

$$B_i' = \frac{b_i}{b} \qquad (5\text{-}23)$$

$$A_i' = \frac{1}{a}\left[2a_i^{0.5}\sum_j^N x_j a_j^{0.5}\left(1-k_{ij}\right)\right] \qquad (5\text{-}24)$$

5.4 <u>Equilibrium Ratio K_{ij}</u>

Calculate K_{ij} from fugacity coefficient

$$\ln\phi_i = -\ln\left[Z - \frac{Pb}{RT}\right] + (Z-1)B_i' - \frac{a}{bRT}\left(A_i' - B_i'\right)\ln\left[1+\frac{Pb}{RTZ}\right] \qquad (5\text{-}25)$$

Liquid Fugacity Coefficient(L)

$$\ln\phi_i^{\,L} = -\ln\left[Z^L - \frac{Pb^L}{RT}\right] + \left(Z^L - 1\right)B_i'^{\,L} - \frac{a^L}{b^L RT}\left(A_i'^{\,L} - B_i'^{\,L}\right)\ln\left[1+\frac{Pb^L}{RTZ^L}\right] \qquad (5\text{-}26)$$

Vapor Fugacity Coefficient(V)

$$\ln\phi_i^{\,V} = -\ln\left[Z^V - \frac{Pb^V}{RT}\right] + \left(Z^V - 1\right)B_i'^{\,V} - \frac{a^V}{b^V RT}\left(A_i'^{\,V} - B_i'^{\,V}\right)\ln\left[1+\frac{Pb^V}{RTZ^V}\right] \qquad (5\text{-}27)$$

then, equation (5-26) - (5-27)

$$\ln\left(\frac{\phi_i^{\,L}}{\phi_i^{\,V}}\right) = -\ln\left[\frac{Z^L - \left(Pb^L/RT\right)}{Z^V - \left(Pb^V/RT\right)}\right] + \left[\left(Z^L - 1\right)B_i'^{\,L} - \left(Z^V - 1\right)B_i'^{\,V}\right.$$

$$-\frac{1}{RT}\left[\frac{a^L}{b^L}\left(A_i'^L - B_i'^L\right)\ln\left[1+\frac{Pb^L}{RTZ^L}\right] - \frac{a^V}{b^V}\left(A_i'^V - B_i'^V\right)\ln\left[1+\frac{Pb^V}{RTZ^V}\right]\right] = U \qquad (5\text{-}28)$$

$$\ln\left(\frac{\phi_i^{\ L}}{\phi_i^{\ V}}\right) = U \qquad (5\text{-}29)$$

$$K_{ij} = \frac{\phi_i^{\ L}}{\phi_i^{\ V}} = \exp(U) \qquad (5\text{-}30)$$

Summary of Equations

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \qquad (5\text{-}1)$$

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z - AB = 0 \qquad (5\text{-}2)$$

where

$$A = \frac{aP}{(RT)^2} \qquad (5\text{-}3)$$

$$B = \frac{bP}{RT} \qquad (5\text{-}4)$$

$$b = \sum^{N} x_i b_i \qquad (5\text{-}5)$$

$$b = 0.08664\,\frac{RT_{ci}}{P_c} \qquad (5\text{-}6)$$

$$a = \sum_i^N \sum_j^N x_i x_j \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right) \qquad (5\text{-}7)$$

$$a_i = a_{ci}\alpha_i \qquad (5\text{-}8)$$

$$a_{ci} = 0.42748\frac{\left(RT_{ci}\right)^2}{P_{ci}} \tag{5-9}$$

$$\alpha_i^{0.5} = 1 + m_i\left(1 - T_{ri}^{0.5}\right) \tag{5-10}$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \tag{5-11}$$

Enthalpy Departure

$$\frac{H - H^*}{RT} = Z - 1 - \frac{1}{bRT}\left[a - T\left(\frac{da}{dT}\right)\right]\ln\left(1 + \frac{b}{V}\right) \tag{5-15}$$

$$\frac{H - H^*}{RT} = Z - 1 - \frac{A}{B}\left[1 - \frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln\left(1 + \frac{B}{Z}\right) \tag{5-16}$$

where

$$T\left(\frac{da}{dT}\right) = -\sum_i^N \sum_j^N x_i x_j m_j \left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1 - k_{ij}\right) \tag{5-17}$$

Fugacity Coefficient

$$\ln\Phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z - 1)B_i' - \frac{a}{bRT}\left(A_i' - B_i'\right)\ln\left(1 + \frac{b}{V}\right) \tag{5-21}$$

$$\ln\Phi_i = -\ln(Z - B) + (Z - 1)B_i' - \frac{A}{B}\left(A_i' - B_i'\right)\ln\left(1 + \frac{B}{Z}\right) \tag{5-22}$$

where

$$B_i' = \frac{b_i}{b} \tag{5-23}$$

$$A_i' = \frac{1}{a}\left[2a_i^{0.5}\sum_j^N x_j a_j^{0.5}\left(1 - k_{ij}\right)\right] \tag{5-24}$$