Implementation of Multi-component Peng–Robinson equation of state in Cantera

Gandhali Kogekar, Steven C. DeCaluwe
Colorado School of Mines

1. Peng-Robinson equation of state

Cantera [1] has already developed a general capability for modeling ideal gas equation of state(EoS) and Redlich-Kwong EoS [2] for multi-component fluid flows. The current paper further extends its capability to include a multi-component, mixture-averaged form of the cubic Peng–Robinson EoS [3]. The P–R EoS implementation presented here generally follows the approach reported by [4] for Redlich-Kwong EoS implementation.

The Peng–Robinson EoS for a pure species is stated as

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2+2bv-b^2}. \tag{1}$$

Here the species-specific, Van der Waals attraction parameter a and repulsive, volume correction parameter b can be calculated as

$$a = \frac{a_0 R^2 T_c^2}{p_c}, b = \frac{b_0 R T_c}{p_c}. \tag{2}$$

Here, T_c and p_c are species-specific critical temperature and pressure respectively. Coefficients a_0 and b_0 in Eq. 2 are calculated based on the solution of a cubic equation are represented as

$$a_0 = 0.45723552888 \tag{3}$$

and

$$b_0 = 0.0777960738922 \tag{4}$$

The detailed derivation of Eqs. 3, 4 are presented in Appendix (A.2).
A temperature dependent interaction parameter α in Eq. 1 is calculated as

$$\alpha(T) = \left[1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2, \tag{5}$$

with the function κ in Eq. 5 is calculated as

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad \text{if} \quad \omega \leq 0.491 \tag{6}$$

$$\kappa = 0.379642 + 1.487503\omega - 0.164423\omega^2 + 0.016666\omega^3 \quad \text{if} \quad \omega > 0.491 \tag{7}$$

Here ω is the acentric factor of the species in question.

2. Multi-component Peng–Robinson EoS

The pure-fluid Peng–Robinson equation of state (Eqs. 1 - 7) can be generalized for a multi-component mixture as

$$p = \frac{RT}{v - b_{\mathrm{mix}}} - \frac{(a\alpha)_{\mathrm{mix}}}{v^2 + 2b_{\mathrm{mix}}v - b_{\mathrm{mix}}^2}. \tag{8}$$

The mixture-averaged parameters a_{mix}, $(a\alpha)_{\mathrm{mix}}$ and b_{mix} are calculated as

$$a_{\mathrm{mix}} = \sum_i \sum_j X_i X_j a_{ij}, \quad b_{\mathrm{mix}} = \sum_i X_i b_i, \quad (a\alpha)_{\mathrm{mix}} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} \tag{9}$$

In the absence of specific inter-species interaction data, the interaction parameters $a_{i,j}$ and $(a\alpha)_{i,j}$ are typically evaluated as the geometric average of the pure-species parameters [5], i.e.

$$a_{ij} = \sqrt{a_i a_j}, (a\alpha)_{i,j} = \sqrt{(a\alpha)_i (a\alpha)_j} \tag{10}$$

Therefore, Eq. 10 can be simplified as

$$a_{\mathrm{mix}} = \sum_i \sum_j X_i X_j a_{ij} = \sum_i \sum_j X_i X_j \sqrt{a_i a_j} \tag{11}$$

$$b_{\mathrm{mix}} = \sum_i X_i b_i \tag{12}$$

$$(a\alpha)_{\mathrm{mix}} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} = \sum_i \sum_j X_i X_j \sqrt{(a\alpha)_i (a\alpha)_j} \tag{13}$$

3. Calculation of Critical properties

From the definitions of coefficients a and b in Eq. 2, critical conditions can be calculated as follows:

$$\frac{a}{b} = \frac{a_0}{b_0} R T_{\mathrm{c}} \tag{14}$$

Species-specific critical temperature T_{c} can be obtained as,

$$T_{\mathrm{c}} = \frac{a b_0}{b a_0 R} \tag{15}$$

Similarly, the critical pressure (p_{c}) and critical volume (v_{c}) are calculated as

$$p_{\mathrm{c}} = \frac{b_0 R}{b} T_{\mathrm{c}} = \frac{a b_0^2}{a_0 b^2} \quad \text{and} \quad v_{\mathrm{c}} = \frac{Z_{\mathrm{c}} R T_{\mathrm{c}}}{p_{\mathrm{c}}} = \frac{b Z_{\mathrm{c}}}{b_0} \tag{16}$$

It should be noted that the critical conditions for a multi-component mixture are obtained using the same equations by replacing species-specific a, b with mixture-averaged parameters a_{mix} and b_{mix}.

4. Helmholtz energy departure function

Derivation of consistent expressions for P-R EoS thermodynamics requires evaluation of the molar Helmholtz free energy A (J mol^{-1}). The molar Helmholtz free energy is defined as

$$p = -\left.\frac{\partial a}{\partial v}\right|_{n_k, T} \tag{17}$$

where n_k is the number of moles of species k, T and p are temperature [K] and pressure [Pa]. Helmholtz energy [J mol^{-1}] and molar volume [m^3 mol^{-1}] are represented by a and v respectively. Integrating Eq. 17 from an ideal-gas reference state (denoted by $^\circ$) to some general state gives

$$\int_{a_o}^{a} da = -\int_{v_o}^{v} pdv \tag{18}$$

Separating integration in two parts, we obtain

$$(a - a^\circ) = \int_{\infty}^{v_0} pdv - \int_{\infty}^{v} pdv \tag{19}$$

Here ∞ represents compression from an infinite molar volume and the reference state v_0 is in the ideal-gas regime. Using ideal gas equation for the integral with v_0, we obtain

$$(a - a^\circ) = \int_{\infty}^{v_0} \frac{RT}{v} dv - \int_{\infty}^{v} pdv \tag{20}$$

Now using P–R EoS for integral with molar volume v yields

$$(a - a^\circ) = \int_{\infty}^{v_0} \frac{RT}{v} dv - \int_{\infty}^{v} \frac{RT}{v-b} dv + \int_{\infty}^{v} \frac{a\alpha}{v^2 + 2bv - b^2} dv \tag{21}$$

Solutions for first and second integrals in Eq. 21 are

$$\int_{\infty}^{v_0} \frac{RT}{v} dv = RT(\ln(v_0) - \ln(\infty)) \quad \text{and} \quad \int_{\infty}^{v} \frac{RT}{v-b} dv = RT(\ln(v-b) - \ln(\infty - b)). \tag{22}$$

The third integral in Eq. 21 evaluates to

$$\int_{\infty}^{v} \frac{a\alpha}{v^2 + 2bv - b^2} dv = \frac{a\alpha}{-2\sqrt{2}b} \left[\ln\left(\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b} \right) - \ln\left(\frac{\infty + (1+\sqrt{2})b}{\infty + (1-\sqrt{2})b} \right) \right]. \tag{23}$$

Note that

$$\ln\left(\frac{\infty + (1+\sqrt{2})b}{\infty + (1-\sqrt{2})b} \right) \approx \ln\left(\frac{\infty}{\infty}\right) \approx \ln(1) = 0. \tag{24}$$

Combining all terms, Eq. 21 simplifies to

$$(a - a^\circ) = RT\ln\left(\frac{v_0}{v-b}\right) - RT\ln\left(\frac{\infty - b}{\infty}\right) + \frac{a\alpha}{-2\sqrt{2}b}\ln\left(\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b} \right). \tag{25}$$

Note that,

$$\ln\left(\frac{\infty - b}{\infty}\right) = \ln\left(1 - \frac{b}{\infty}\right) \approx \ln(1-0) = 0 \tag{26}$$

Therefore,

$$(a - a^\circ) = RT\ln\left(\frac{v_0}{v-b}\right) + \frac{a\alpha}{-2\sqrt{2}b}\ln\left(\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b} \right). \tag{27}$$

Helmholtz energy is thus represented as

$$a = a^\circ - RT\ln\left(\frac{v-b}{v_0}\right) - \frac{a\alpha}{2\sqrt{2}b}\ln\left(\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b} \right) \tag{28}$$

The total Helmholtz energy is given as

$$A = na = na^\circ - nRT\ln\left(\frac{V-nb}{V_0}\right) - \frac{na\alpha}{2\sqrt{2}b}\ln\left(\frac{V + (1+\sqrt{2})nb}{V + (1-\sqrt{2})nb} \right) \tag{29}$$

where V is the total volume ($V = nv$) and n is a total number of moles of individual species.

5. Helmholtz energy for multi-component mixture

Total Helmholtz energy for n_T moles (of a multi-component mixture) can be calculated as

$$A_{\mathrm{mix}} = n_{\mathrm{T}} a_{\mathrm{mix}} = \sum_i n_i a_i \tag{30}$$

Separating ideal and excess parts,

$$A_{\mathrm{mix}} = \sum_i n_i (a_i^{\circ} + a_i^{r}) = \sum_i n_i (a_i^{\circ}) + \sum_i n_i (a_i - a_i^{\circ}) \tag{31}$$

Using Eq. 27, we get

$$n_{\mathrm{T}} a_{\mathrm{mix}} = \sum_i n_i a_i^{\circ} + \sum_i n_i \left[RT \ln \left(\frac{V_0}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} \right) - \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln \left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \right] \tag{32}$$

Using Ideal gas EoS, we obtain

$$V_0 = \frac{nRT}{p^{\circ}} \tag{33}$$

Substituting Eq. 33 in Eq. 32,

$$n_{\mathrm{T}} a_{\mathrm{mix}} = \sum_i n_i a_i^{\circ} + \sum_i n_i \left[RT \ln \left(\frac{n_i RT}{p^{\circ} (V - n_{\mathrm{T}} b_{\mathrm{mix}})} \right) - \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln \left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \right] \tag{34}$$

Helmholtz energy of a multi-component mixture can be stated as

$$\begin{aligned} n_{\mathrm{T}} a_{\mathrm{mix}} = \sum_i n_i a_i^{\circ} - \sum_i n_i RT \ln \left(\frac{p^{\circ} V}{n_i RT} \right) + n_{\mathrm{T}} RT \ln \left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \\ - n_{\mathrm{T}} \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln \left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \end{aligned} \tag{35}$$

6. Chemical Potential for multi-component mixture

Using the molar Helmholtz energy function (Eq. 35), other energy departure functions can be defined according to the thermodynamic relationships. The present section focuses on the derivation of the chemical potential μ_k, which further leads to a definition of an activity coefficient γ_k. The chemical potential μ_k for a species k is defined as

$$\mu_i = \left. \frac{d(n_{\mathrm{T}} A)}{d n_i} \right|_{T, V, n_j} \tag{36}$$

Total Helmholtz energy given by Eq. 35 is

$$\begin{aligned} n_{\mathrm{T}} a_{\mathrm{mix}} = \sum_i n_i a_i^{\circ} - \sum_i n_i RT \ln \left(\frac{p^{\circ} V}{n_i RT} \right) + n_{\mathrm{T}} RT \ln \left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \\ - n_{\mathrm{T}} \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln \left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}} \right) \end{aligned} \tag{37}$$

Taking derivative with respect to number of moles (n_i) of i^{th} species, we obtain

$$\begin{aligned}\mu_i = a_i^\circ - RT\ln\left(\frac{p^\circ V}{n_i RT}\right) + n_i RT\frac{n_i RT}{p^\circ V}\frac{p^\circ V}{n_i^2 RT} + RT\ln\left(\frac{V}{V - n_{\mathrm{T}}b_{\mathrm{mix}}}\right) + \\ n_{\mathrm{T}}RT\frac{V - n_{\mathrm{T}}b_{\mathrm{mix}}}{V}\frac{Vb_i}{(V - n_{\mathrm{T}}b_{\mathrm{mix}})^2} \\ -\frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right]\end{aligned} \tag{38}$$

Simplification of above equation yields

$$\begin{aligned}\mu_i = a_i^\circ - RT\ln\left(\frac{p^\circ V}{n_i RT}\right) + RT + RT\ln\left(\frac{V}{V - n_{\mathrm{T}}b_{\mathrm{mix}}}\right) + \frac{b_i n_{\mathrm{T}}RT}{(V - n_{\mathrm{T}}b_{\mathrm{mix}})} \\ -\frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right]\end{aligned} \tag{39}$$

Recalling that $\mu_i^\circ = a_i^\circ + RT$,

$$\begin{aligned}\mu_i = \mu_i^\circ - RT\ln\left(\frac{p^\circ}{p}\right) - RT\ln\left(\frac{pV}{n_i RT}\right) + RT\ln\left(\frac{V}{V - n_{\mathrm{T}}b_{\mathrm{mix}}}\right) + \frac{b_i n_{\mathrm{T}}RT}{(V - n_{\mathrm{T}}b_{\mathrm{mix}})} \\ -\frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right]\end{aligned} \tag{40}$$

Simplifying further,

$$\begin{aligned}\mu_i = \mu_i(T)^\circ - RT\ln\left(\frac{p^\circ}{p}\right) + RT\ln(X_i) - RT\ln\left(\frac{pV}{n_{\mathrm{T}}RT}\right) + RT\ln\left(\frac{V}{V - n_{\mathrm{T}}b_{\mathrm{mix}}}\right) \\ +\frac{b_i n_{\mathrm{T}}RT}{(V - n_{\mathrm{T}}b_{\mathrm{mix}})} - \frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right]\end{aligned} \tag{41}$$

The last term in above equation is calculated as

$$\begin{aligned}\frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right] = \left[\frac{2\sum_j n_j (a\alpha)_{ij}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}} - \frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}b_i}{2\sqrt{2}n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2}\right]\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right) \\ +\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\left(\frac{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\frac{(V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})(1+\sqrt{2})b_i - (V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})(1-\sqrt{2})b_i}{(V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})^2}\end{aligned} \tag{42}$$

Simplifying above equation, we get

$$\begin{aligned}\frac{d}{dn_i}\left[\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\right] \\ = \left[\frac{2\sum_j n_j (a\alpha)_{ij}}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}} - \frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}b_i}{2\sqrt{2}n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2}\right]\ln\left(\frac{V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right) \\ +\frac{(n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}b_i V}{(V + (1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})(V + (1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})(n_{\mathrm{T}}b_{\mathrm{mix}})}\end{aligned} \tag{43}$$

Hence chemical potential for a species i in a multi-component mixture is represented as

$$\mu_i = \mu_i(T)^\circ - RT\ln\left(\frac{p^\circ}{p}\right) + RT\ln(X_i) - RT\ln\left(\frac{pV}{n_\mathrm{T}RT}\right) + RT\ln\left(\frac{V}{V - n_\mathrm{T}b_\mathrm{mix}}\right) + \frac{b_i n_\mathrm{T}RT}{(V - n_\mathrm{T}b_\mathrm{mix})} - \left[\frac{2\sum_j n_j(a\alpha)_{ij}}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}} - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i}{2\sqrt{2}n_\mathrm{T}^2 b_\mathrm{mix}^2}\right]\ln\left(\frac{V + (1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V + (1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right) - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i V}{(V^2 + 2n_\mathrm{T}Vb_\mathrm{mix} - n_\mathrm{T}^2 b_\mathrm{mix}^2)n_\mathrm{T}b_\mathrm{mix}} \tag{44}$$

6.1 Activity coefficients of a multi-component mixture

The species activity (α_i) is defined as

$$\alpha_i = \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right) \tag{45}$$

Substituting definition of α_i in Eq. 44, we get

$$RT\ln(\alpha_i) = -RT\ln\left(\frac{p^\circ}{p}\right) + RT\ln(X_i) - RT\ln\left(\frac{pV}{n_\mathrm{T}RT}\right) + RT\ln\left(\frac{V}{V - n_\mathrm{T}b_\mathrm{mix}}\right) + \frac{b_i n_\mathrm{T}RT}{(V - n_\mathrm{T}b_\mathrm{mix})} - \left[\frac{2\sum_j n_j(a\alpha)_{ij}}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}} - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i}{2\sqrt{2}n_\mathrm{T}^2 b_\mathrm{mix}^2}\right]\ln\left(\frac{V + (1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V + (1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right) - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i V}{(V^2 + 2n_\mathrm{T}Vb_\mathrm{mix} - n_\mathrm{T}^2 b_\mathrm{mix}^2)n_\mathrm{T}b_\mathrm{mix}} \tag{46}$$

Note that

$$-RT\ln\left(\frac{p^\circ}{p}\right) + RT\ln(X_i) - RT\ln\left(\frac{pV}{n_\mathrm{T}RT}\right) = RT\ln\left(\frac{[C_i]}{[C^\circ]}\right) \tag{47}$$

where $[C^\circ] = p^\circ/RT$ is the reference concentration and $[C_i] = pX_i/RT$ is the concentration of species i. The activity coefficient γ_i is defined as

$$\gamma_i = \frac{\alpha_i[C^\circ]}{[C_i]} \tag{48}$$

Therefore Eq. 44 reduces to

$$RT\ln(\gamma_i) = -RT\ln\left(\frac{pV}{n_\mathrm{T}RT}\right) + RT\ln\left(\frac{V}{V - n_\mathrm{T}b_\mathrm{mix}}\right) + \frac{b_i n_\mathrm{T}RT}{(V - n_\mathrm{T}b_\mathrm{mix})} - \left[\frac{2\sum_j n_j(a\alpha)_{ij}}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}} - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i}{2\sqrt{2}n_\mathrm{T}^2 b_\mathrm{mix}^2}\right]\ln\left(\frac{V + (1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V + (1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right) - \frac{(n_\mathrm{T}^2 a\alpha)_\mathrm{mix}b_i V}{(V^2 + 2n_\mathrm{T}Vb_\mathrm{mix} - n_\mathrm{T}^2 b_\mathrm{mix}^2)n_\mathrm{T}b_\mathrm{mix}} \tag{49}$$

7. Entropy for multi-component mixture

Entropy of a multi-component mixture can be expressed as

$$n_\mathrm{T}S = -\left.\frac{d(n_\mathrm{T}A)}{dT}\right|_{V,n_i} \tag{50}$$

Using Eq. 35 for Helmholtz energy, total entropy can be obtained as

$$n_\mathrm{T}s_\mathrm{mix} = \sum_i n_i s_i^\circ + \sum_i n_i R\ln\left(\frac{p^\circ V}{n_i RT}\right) + \sum_i n_i RT\left(\frac{n_i RT}{p^\circ V}\right)\left(\frac{p^\circ V}{n_i R}\right)\left(\frac{-1}{T^2}\right) - n_\mathrm{T}R\ln\left(\frac{V}{V - n_\mathrm{T}b_\mathrm{mix}}\right) + \frac{n_\mathrm{T}}{2\sqrt{2}b_\mathrm{mix}}\ln\left(\frac{V + (1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V + (1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\frac{\partial(a\alpha)_\mathrm{mix}}{\partial T} \tag{51}$$

The reference state entropy is given by

$$S_i^\circ = -\frac{da_i^\circ}{dT} \tag{52}$$

Simplification yields,

$$\begin{aligned} n_\mathrm{T} s_\mathrm{mix} = \sum_i n_i s_i^\circ + \sum_i n_i R \ln\left(\frac{p^\circ V}{n_i RT}\right) - \sum_i n_i R - n_\mathrm{T} R \ln\left(\frac{V}{V - n_\mathrm{T} b_\mathrm{mix}}\right) \\ + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln\left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}\right) \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T} \end{aligned} \tag{53}$$

Adding and subtracting $\sum n_i R \ln(p)$ term, we obtain

$$\begin{aligned} n_\mathrm{T} s_\mathrm{mix} = \sum_i n_i s_i^\circ + \sum_i n_i R \ln\left(\frac{p^\circ}{p}\right) + \sum_i n_i R \ln\left(\frac{pV}{n_i RT}\right) - n_\mathrm{T} R - n_\mathrm{T} R \ln\left(\frac{V}{V - n_\mathrm{T} b_\mathrm{mix}}\right) \\ + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln\left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}\right) \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T} \end{aligned} \tag{54}$$

Now using the fact, $n_i = X_i n_\mathrm{T}$ and $pV = Z n_\mathrm{T} RT$,

$$\begin{aligned} n_\mathrm{T} s_\mathrm{mix} = \sum_i n_i s_i^\circ + n_\mathrm{T} R \ln\left(\frac{p^\circ}{p}\right) + \sum_i n_i R \ln\left(\frac{Z}{X_i}\right) - n_\mathrm{T} R - n_\mathrm{T} R \ln\left(\frac{V}{V - n_\mathrm{T} b_\mathrm{mix}}\right) \\ + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln\left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}\right) \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T} \end{aligned} \tag{55}$$

Considering that reference (or standard) states are evaluated at constant pressure, and the derivative for entropy term is perfomed at constant volume (Eq. 50), the term $n_\mathrm{T} R$ needs to be ignored [4]. Therefore total entropy for a multi-component mixture is stated as

$$\begin{aligned} n_\mathrm{T} s_\mathrm{mix} = \sum_i n_i s_i^\circ + n_\mathrm{T} R \ln\left(\frac{p^\circ}{p}\right) - \sum_i n_i R \ln(X_i) + n_\mathrm{T} R \ln(Z) - n_\mathrm{T} R \ln\left(\frac{V}{V - n_\mathrm{T} b_\mathrm{mix}}\right) \\ + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln\left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}\right) \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T}. \end{aligned} \tag{56}$$

The ideal gas contribution to the entropy is

$$n_\mathrm{T} s_\mathrm{mix}^\circ = \sum_i n_i s_i^\circ + n_\mathrm{T} R \ln\left(\frac{p^\circ}{p}\right) - \sum_i n_i R \ln(X_i) \tag{57}$$

and the non-ideal contribution becomes

$$n_\mathrm{T} s_\mathrm{mix}^r = n_\mathrm{T} R \ln(Z) - n_\mathrm{T} R \ln\left(\frac{V}{V - n_\mathrm{T} b_\mathrm{mix}}\right) + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln\left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}\right) \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T}. \tag{58}$$

8. Internal energy

Internal energy is expressed as:

$$n_\mathrm{T} u = n_\mathrm{T}(a + Ts) \tag{59}$$

Using Eqs. 35 and 53,

$$
\begin{aligned}
n_{\mathrm{T}} u_{\mathrm{mix}} = \sum_i n_i a_i^{\circ} - \sum_i n_i RT \ln\left(\frac{p^{\circ} V}{n_i RT}\right) + n_{\mathrm{T}} RT \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \\
- n_{\mathrm{T}} \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) + \sum_i n_i s_i^{\circ} T + n_{\mathrm{T}} RT \ln\left(\frac{p^{\circ}}{p}\right) \\
+ \sum_i n_i RT \ln\left(\frac{pV}{n_i RT}\right) - n_{\mathrm{T}} RT \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \\
+ T \frac{n_{\mathrm{T}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T}
\end{aligned} \tag{60}
$$

Note that,

$$u_i^{\circ} = n_i (a_i^{\circ} + T s_i^{\circ}) \tag{61}$$

Canceling common terms,

$$
\begin{aligned}
n_{\mathrm{T}} u_{\mathrm{mix}} = \sum_i n_i u_i^{\circ} - \cancel{\sum_i n_i RT \ln\left(\frac{p^{\circ} V}{n_i RT}\right)} + \cancel{n_{\mathrm{T}} RT \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right)} \\
- n_{\mathrm{T}} \frac{(a\alpha)_{\mathrm{mix}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) + \cancel{\sum_i n_i RT \ln\left(\frac{p^{\circ} V}{n_i RT}\right)} \\
\cancel{- n_{\mathrm{T}} RT \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right)} + T \frac{n_{\mathrm{T}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T}
\end{aligned} \tag{62}
$$

The equation for internal energy simplifies to

$$n_{\mathrm{T}} u_{\mathrm{mix}} = \sum_i n_i u_i^{\circ} + \frac{n_{\mathrm{T}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left[T \frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T} - (a\alpha)_{\mathrm{mix}}\right] \tag{63}$$

9. Enthalpy

The total mixture enthalpy is calculated as

$$n_{\mathrm{T}} h = n_{\mathrm{T}} u + pV \tag{64}$$

Using Eq. 63, the mixture enthalpy becomes

$$n_{\mathrm{T}} h_{\mathrm{mix}} = \sum_i n_i u_i^{\circ} + \frac{n_{\mathrm{T}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left[T \frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T} - (a\alpha)_{\mathrm{mix}}\right] + pV \tag{65}$$

Note that

$$n_i h_i^{\circ} = n_i u_i^{\circ} + p V_i^{\circ} = n_i u_i^{\circ} + n_i RT \tag{66}$$

Therefore expression for mixure enthalpy can be stated as

$$n_{\mathrm{T}} h_{\mathrm{mix}} = \sum_i n_i h_i^{\circ} - n_{\mathrm{T}} RT + pV + \frac{n_{\mathrm{T}}}{2\sqrt{2} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left[T \frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T} - (a\alpha)_{\mathrm{mix}}\right] \tag{67}$$

10. Gibb's Free Energy

Gibb's Free Energy is calculated as

$$n_{\mathrm{T}}G_{\mathrm{mix}} = n_{\mathrm{T}}h_{\mathrm{mix}} - n_{\mathrm{T}}Ts_{\mathrm{mix}} \tag{68}$$

Separating the ideal and non-ideal parts, we obtain

$$n_{\mathrm{T}}G_{\mathrm{mix}} = (n_{\mathrm{T}}h^{\circ}_{\mathrm{mix}} - n_{\mathrm{T}}Ts^{\circ}_{\mathrm{mix}}) + (n_{\mathrm{T}}h^{r}_{\mathrm{mix}} - n_{\mathrm{T}}Ts^{r}_{\mathrm{mix}}) \tag{69}$$

The ideal-gas contribution for the Gibbs energy can be defined as

$$n_{\mathrm{T}}G^{\circ}_{\mathrm{mix}} = n_{\mathrm{T}}h^{\circ}_{\mathrm{mix}} - n_{\mathrm{T}}Ts^{\circ}_{\mathrm{mix}} \tag{70}$$

Using Eq. 67 and Eq. 56, the residual part can be written as,

$$\begin{aligned} n_{\mathrm{T}}G_{\mathrm{mix}} = {} & -n_{\mathrm{T}}RT + pV + \frac{n_{\mathrm{T}}}{2\sqrt{2}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{\partial(a\alpha)_{\mathrm{mix}}}{\partial T} - (a\alpha)_{\mathrm{mix}}\right] \\ & -T\left[n_{\mathrm{T}}R\ln(Z) - n_{\mathrm{T}}R\ln\left(\frac{V}{V-n_{\mathrm{T}}b_{\mathrm{mix}}}\right) + \frac{n_{\mathrm{T}}}{2\sqrt{2}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\frac{\partial(a\alpha)_{\mathrm{mix}}}{\partial T}\right]. \end{aligned} \tag{71}$$

Simplification yields,

$$\begin{aligned} n_{\mathrm{T}}G_{\mathrm{mix}} = {} & -n_{\mathrm{T}}RT + pV - \frac{n_{\mathrm{T}}(a\alpha)_{\mathrm{mix}}}{2\sqrt{2}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right) \\ & -n_{\mathrm{T}}RT\ln(Z) + n_{\mathrm{T}}RT\ln\left(\frac{V}{V-n_{\mathrm{T}}b_{\mathrm{mix}}}\right). \end{aligned} \tag{72}$$

The ideal gas contribution to the Gibb's energy is

$$n_{\mathrm{T}}G_{\mathrm{mix}} = \sum_i n_i g^{\circ}_i + n_{\mathrm{T}}RT\ln\left(\frac{p^{\circ}}{p}\right) - T\sum_i n_i\ln(X_i) \tag{73}$$

and the non-ideal contribution is

$$\begin{aligned} n_{\mathrm{T}}G_{\mathrm{mix}} = {} & RT(Z-1) - \frac{(a\alpha)_{\mathrm{mix}}n_{\mathrm{T}}}{2\sqrt{2}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right) \\ & -n_{\mathrm{T}}RT\ln(Z) + n_{\mathrm{T}}RT\ln\left(\frac{V}{V-n_{\mathrm{T}}b_{\mathrm{mix}}}\right). \end{aligned} \tag{74}$$

11. Specific heat capacities

11.1 Specific heat capacity at constant pressure, C_{p}

Specific heat capacity at constant pressure is calculated as:

$$C_{\mathrm{p}} = \left.\frac{dH}{dT}\right|_{V,n_i} - \left[V + T\frac{\left(\frac{dp}{dT}\right)_{n_i,V}}{\left(\frac{dp}{dV}\right)_{n_i,T}}\right]\left.\frac{dp}{dT}\right|_{n_i,V} \tag{75}$$

Using expression for total enthalpy (Eq. 67),

$$H = n_\mathrm{T} h_\mathrm{mix} = \sum_i n_i h_i^\circ - n_\mathrm{T} RT + pV + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln \left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}} \right) \left[T \frac{\partial (a\alpha)_\mathrm{mix}}{\partial T} - (a\alpha)_\mathrm{mix} \right] \tag{76}$$

Taking derivative with respect to temperature T,

$$\left.\frac{dH}{dT}\right|_{V,n_i} = \sum_i n_i c_{p,i}^\circ - n_\mathrm{T} R + \frac{\partial p}{\partial T} V + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln \left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}} \right) \left(T \frac{\partial^2 (a\alpha)_\mathrm{mix}}{\partial T^2} \right) \tag{77}$$

Using Eq.s 75 and 77, the specific heat capacity at constant pressure is evaluated as

$$\begin{aligned} c_\mathrm{p} = \sum_i n_i c_{p,i}^\circ - n_\mathrm{T} R + \frac{\partial p}{\partial T} V + \frac{n_\mathrm{T}}{2\sqrt{2} b_\mathrm{mix}} \ln \left(\frac{V + (1+\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}}{V + (1-\sqrt{2}) n_\mathrm{T} b_\mathrm{mix}} \right) \left(T \frac{\partial^2 (a\alpha)_\mathrm{mix}}{\partial T^2} \right) \\ - \left[V + T \frac{\left(\frac{dp}{dT}\right)_{n_i,V}}{\left(\frac{dp}{dV}\right)_{n_i,T}} \right] \left.\frac{dp}{dT}\right|_{n_i,V} \end{aligned} \tag{78}$$

11.2 Specific heat capacity at constant volume, C_v

Specific heat capacity at constant volume can be calculated using Eq. 78 and other pressure derivatives as

$$c_\mathrm{v} = c_\mathrm{p} + T \left[\frac{\left(\frac{dp}{dT}\right)_{n_i,V}}{\left(\frac{dp}{dV}\right)_{n_i,T}} \right] \left.\frac{dp}{dT}\right|_{n_i,V} \tag{79}$$

The calculations of all pressure derivatives in Eq. 79 are presented in Appendix (A.6).

12. Partial molar properties

Calculation of partial molar properties follows the approach described in Sandia report [4].

12.1 Partial molar volumes

The Peng-Robinson EoS (Eq. 8) can be rearranged as

$$pV = n_\mathrm{T} RT \left(1 + \frac{n_\mathrm{T} b_\mathrm{mix}}{V - n_\mathrm{T} b_\mathrm{mix}} \right) - \frac{n_\mathrm{T}^2 (a\alpha)_\mathrm{mix} V}{V^2 + 2 b_\mathrm{mix} n_\mathrm{T} V - b_\mathrm{mix}^2 n_\mathrm{T}^2} \tag{80}$$

Species-specific partial molar volumes are defined as:

$$V_i = \left.\frac{dV}{dn_i}\right|_{T,p,n_j} \tag{81}$$

Differentiating Eq. 80,

$$\begin{aligned} p\frac{dV}{dn_i} = RT \left(1 + \frac{n_\mathrm{T} b_\mathrm{mix}}{V - n_\mathrm{T} b_\mathrm{mix}} \right) + n_\mathrm{T} RT \left(\frac{b_i}{V - n_\mathrm{T} b_\mathrm{mix}} - \frac{n_\mathrm{T} b_\mathrm{mix}}{(V - n_\mathrm{T} b_\mathrm{mix})^2} \left(\frac{dV}{dn_i} - b_i \right) \right) \\ - \frac{2 \sum_j n_j (a\alpha)_{ij} V}{V^2 + 2 b_\mathrm{mix} n_\mathrm{T} V - b_\mathrm{mix}^2 n_\mathrm{T}^2} - \frac{dV}{dn_i} \frac{n_\mathrm{T}^2 (a\alpha)_\mathrm{mix}}{V^2 + 2 b_\mathrm{mix} n_\mathrm{T} V - b_\mathrm{mix}^2 n_\mathrm{T}^2} \\ + \frac{n_\mathrm{T}^2 (a\alpha)_\mathrm{mix} V}{(V^2 + 2 b_\mathrm{mix} n_\mathrm{T} V - b_\mathrm{mix}^2 n_\mathrm{T}^2)^2} \left(2V \frac{\partial V}{\partial n_i} + 2 b_i V + 2 b_\mathrm{mix} n_\mathrm{T} \frac{\partial V}{\partial n_i} - 2 b_\mathrm{mix} n_\mathrm{T} b_i \right) \end{aligned} \tag{82}$$

Collecting common terms yields,

$$
\begin{aligned}
p\frac{dV}{dn_i} = RT + \frac{n_{\mathrm{T}}b_{\mathrm{mix}}RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTb_i}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} - \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2}\left(\frac{dV}{dn_i} - b_i\right) \\
-\frac{2\sum_j n_j(a\alpha)_{ij}V}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} - \frac{dV}{dn_i}\frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} \\
+\frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}\left(2V\frac{\partial V}{\partial n_i} + 2b_iV + 2b_{\mathrm{mix}}n_{\mathrm{T}}\frac{\partial V}{\partial n_i} - 2b_{\mathrm{mix}}n_{\mathrm{T}}b_i\right)
\end{aligned}
\tag{83}
$$

$$
\begin{aligned}
p\frac{dV}{dn_i} + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2}\frac{dV}{dn_i} + \frac{dV}{dn_i}\frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} \\
-\frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}\left(2V\frac{\partial V}{\partial n_i} + 2b_{\mathrm{mix}}n_{\mathrm{T}}\frac{\partial V}{\partial n_i}\right) \\
= RT + \frac{n_{\mathrm{T}}b_{\mathrm{mix}}RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTb_i}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}b_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} \\
-\frac{2\sum_j n_j(a\alpha)_{ij}V}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} + \frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}(2b_iV - 2b_{\mathrm{mix}}n_{\mathrm{T}}b_i)
\end{aligned}
\tag{84}
$$

Hence,

$$
\begin{aligned}
\frac{dV}{dn_i}\left(p + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} + \frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} - \frac{(2V+2b_{\mathrm{mix}}n_{\mathrm{T}})n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}\right) = \\
RT + \frac{n_{\mathrm{T}}b_{\mathrm{mix}}RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTb_i}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}b_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} \\
-\frac{2\sum_j n_j(a\alpha)_{ij}V}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} + \frac{2b_in_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V(V-b_{\mathrm{mix}}n_{\mathrm{T}})}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}
\end{aligned}
\tag{85}
$$

Partial molar volumes are then given as:

$$
\frac{dV}{dn_i} = \frac{RT + \frac{n_{\mathrm{T}}b_{\mathrm{mix}}RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{b_in_{\mathrm{T}}RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}b_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} - \frac{2\sum_j n_j(a\alpha)_{ij}V}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} + \frac{2b_in_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V(V-b_{\mathrm{mix}}n_{\mathrm{T}})}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}}{\left(p + \frac{n_{\mathrm{T}}RTn_{\mathrm{T}}b_{\mathrm{mix}}}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} + \frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} - \frac{(2V+2b_{\mathrm{mix}}n_{\mathrm{T}})n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}\right)}
\tag{86}
$$

Simplifying,

$$
\frac{dV}{dn_i} = \frac{RT(1 + n_{\mathrm{T}}\frac{(b_{\mathrm{mix}}+b_i)}{V-n_{\mathrm{T}}b_{\mathrm{mix}}} + n_{\mathrm{T}}^2\frac{b_{\mathrm{mix}}b_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2}) - \frac{2\sum_j n_j(a\alpha)_{ij}V}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} + \frac{2b_in_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V(V-b_{\mathrm{mix}}n_{\mathrm{T}})}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}}{\left(p + \frac{n_{\mathrm{T}}^2RTb_{\mathrm{mix}}}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2} + \frac{n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}}{V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2} - \frac{(2V+2b_{\mathrm{mix}}n_{\mathrm{T}})n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}V}{(V^2+2b_{\mathrm{mix}}n_{\mathrm{T}}V-b_{\mathrm{mix}}^2n_{\mathrm{T}}^2)^2}\right)}
\tag{87}
$$

12.2 Partial molar enthalpy

Total enthalpy is given by Eq. 67

$$
\begin{aligned}
n_{\mathrm{T}}h_{\mathrm{mix}} = \sum_i n_ih_i^\circ - n_{\mathrm{T}}RT + pV \\
+\frac{n_{\mathrm{T}}}{2\sqrt{2}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d(a\alpha)_{\mathrm{mix}}}{dT} - (a\alpha)_{\mathrm{mix}}\right]
\end{aligned}
\tag{88}
$$

This equation can be rewritten as

$$n_{\mathrm{T}}h_{\mathrm{mix}} = \sum_i n_i h_i^\circ - n_{\mathrm{T}}RT + pV$$
$$+\frac{1}{2\sqrt{2}b_{\mathrm{mix}}n_{\mathrm{T}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - n_{\mathrm{T}}^2(a\alpha)_{\mathrm{mix}}\right] \tag{89}$$

Partial molar enthalpy is calculated as:

$$h_i = \left.\frac{d(n_{\mathrm{T}}h_{\mathrm{mix}})}{dn_i}\right|_{p,T,n_j} \tag{90}$$

Above derivative at constant pressure is calculated using

$$\left.\frac{dn_{\mathrm{T}}h}{dn_i}\right|_{p,T,n_j} = \left.\frac{dn_{\mathrm{T}}h}{dn_i}\right|_{V,T,n_j} - \left[V + T\frac{\left.\frac{dp}{dT}\right|_{n_i,V}}{\left.\frac{dp}{dV}\right|_{n_i,T}}\right]\left.\frac{dp}{dn_i}\right|_{V,T,n_j} \tag{91}$$

Hence

$$\left.\frac{d(n_{\mathrm{T}}h)}{dn_i}\right|_{T,V,n_j} = h_i^\circ - RT + V\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}n_{\mathrm{T}}^2b_{\mathrm{mix}}^2}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - (n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}\right]$$
$$+\frac{1}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\left(\frac{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left(\frac{((1+\sqrt{2})b_i(V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}) - (1-\sqrt{2})b_i(V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}))}{(V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})^2}\right)$$
$$\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - (n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}\right]$$
$$+\frac{1}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\frac{d}{dn_i}\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - (n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}\right] \tag{92}$$

Consider the term

$$\left.\frac{d(n_{\mathrm{T}}h)}{dn_i}\right|_{T,V,n_j} = h_i^\circ - RT + V\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}n_{\mathrm{T}}^2b_{\mathrm{mix}}^2}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - (n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}\right]$$
$$+\frac{1}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\left(\frac{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left(\frac{((1+\sqrt{2})b_i(V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}) - (1-\sqrt{2})b_i(V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}))}{(V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}})^2}\right)$$
$$\left[T\frac{d(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{dT} - (n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}\right]$$
$$+\frac{1}{2\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d(2\sum_j n_j(a\alpha)_{ij})}{dT} - 2\sum_j n_j(a\alpha)_{ij}\right] \tag{93}$$

Note that

$$\frac{\partial(n_{\mathrm{T}}^2a\alpha)_{\mathrm{mix}}}{\partial n_k} = 2\sum_j n_j(a\alpha)_{kj} \tag{94}$$

$$\frac{d(2\sum_j n_j(a\alpha)_{ij})}{dT} = 2\sum_j n_j \frac{d(a\alpha)_{i,j}}{dT} = \sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right) \tag{95}$$

Simplifying,

$$\begin{aligned}\left.\frac{d(n_\mathrm{T}h)}{dn_i}\right|_{T,V,n_j} = h_i^\circ - RT + V\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}b_\mathrm{mix}^2}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\frac{d(a\alpha)_\mathrm{mix}}{dT} - (a\alpha)_\mathrm{mix}\right] \\ + \frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\left(\frac{2\sqrt{2}Vb_i}{V^2+2n_\mathrm{T}b_\mathrm{mix}V - n_\mathrm{T}^2b_\mathrm{mix}^2}\right)\left[T\frac{d(n_\mathrm{T}^2a\alpha)_\mathrm{mix}}{dT} - (n_\mathrm{T}^2a\alpha)_\mathrm{mix}\right] \\ + \frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right) - 2\sum_j n_j(a\alpha)_{ij}\right]\end{aligned} \tag{96}$$

Hence,

$$\begin{aligned}\left.\frac{d(n_\mathrm{T}h)}{dn_i}\right|_{T,V,n_j} = h_i^\circ - RT + V\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}b_\mathrm{mix}^2}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\frac{d(a\alpha)_\mathrm{mix}}{dT} - (a\alpha)_\mathrm{mix}\right] \\ + \frac{n_\mathrm{T}}{b_\mathrm{mix}}\left(\frac{Vb_i}{V^2+2n_\mathrm{T}b_\mathrm{mix}V - n_\mathrm{T}^2b_\mathrm{mix}^2}\right)\left[T\frac{d(n_\mathrm{T}^2a\alpha)_\mathrm{mix}}{dT} - (n_\mathrm{T}^2a\alpha)_\mathrm{mix}\right] \\ + \frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right) - 2\sum_j n_j(a\alpha)_{ij}\right]\end{aligned} \tag{97}$$

12.3 Partial molar entropy

Partial molar entropy is calculated as:

$$s_i = \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dn_i}\right|_{p,T,n_j} \tag{98}$$

First, consider

$$\left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dn_i}\right|_V = \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dn_i}\right|_p + \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{p}\right|_{n_i}\left.\frac{dp}{dn_i}\right|_V \tag{99}$$

The partial molar entropy s_i can be expressed as

$$s_i = \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dn_i}\right|_{p,T,n_j} = \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dn_i}\right|_{V,T,n_j} - \left.\frac{d(n_\mathrm{T}s_\mathrm{mix})}{dp}\right|_{n_i}\left.\frac{dp}{dn_i}\right|_{V,T,n_j} \tag{100}$$

Total entropy is given by Eq. 53 as

$$\begin{aligned}n_\mathrm{T}s_\mathrm{mix} = \sum_i n_i s_i^\circ + \sum_i n_i R\ln\left(\frac{p^\circ V}{n_i RT}\right) - n_\mathrm{T}R - n_\mathrm{T}R\ln\left(\frac{V}{V-n_\mathrm{T}b_\mathrm{mix}}\right) \\ + \frac{n_\mathrm{T}}{2\sqrt{2}b_\mathrm{mix}}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\frac{\partial(a\alpha)_\mathrm{mix}}{\partial T}.\end{aligned} \tag{101}$$

The above equation can be rewritten as

$$
\begin{aligned}
n_{\mathrm{T}} s_{\mathrm{mix}} = \sum_i n_i s_i^\circ + \sum_i n_i R \ln\left(\frac{p^\circ V}{n_i RT}\right) - n_{\mathrm{T}} R - n_{\mathrm{T}} R \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \\
+ \frac{1}{2\sqrt{2} n_{\mathrm{T}} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T}.
\end{aligned}
\tag{102}
$$

Ignoring the term $n_{\mathrm{T}} R$ as previously discussed and taking derivative of Eq. 53 with respect to n_i at constant volume and temperature, we obtain

$$
\begin{aligned}
\left.\frac{n_{\mathrm{T}} s_{\mathrm{mix}}}{dn_i}\right|_{V,T,n_j} = s_i^\circ + R \ln\left(\frac{p^\circ V}{n_i RT}\right) + n_i R \left(\frac{n_i RT}{p^\circ V}\right) \frac{p^\circ V}{RT} \left(\frac{-1}{n_i^2}\right) - R \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \\
- n_{\mathrm{T}} R \left(\frac{V - n_{\mathrm{T}} b_{\mathrm{mix}}}{V}\right) \frac{-V b_i}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})^2} - \frac{b_i}{2\sqrt{2} (b_{\mathrm{mix}})^2} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} \\
+ \frac{b_i}{2\sqrt{2} n_{\mathrm{T}} b_{\mathrm{mix}}} \left(\frac{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left(\frac{(1+\sqrt{2})(V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}) - (1-\sqrt{2})(V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}})}{(V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}})^2}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} \\
+ \frac{1}{2\sqrt{2} n_{\mathrm{T}} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{d}{dn_i}\left[\frac{d (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{dT}\right]
\end{aligned}
\tag{103}
$$

Simplifying, we get

$$
\begin{aligned}
\left.\frac{n_{\mathrm{T}} s_{\mathrm{mix}}}{dn_i}\right|_{V,T,n_j} = s_i^\circ + R \ln\left(\frac{p^\circ V}{n_i RT}\right) - R - R \ln\left(\frac{V}{V - n_{\mathrm{T}} b_{\mathrm{mix}}}\right) + \frac{n_{\mathrm{T}} R b_i}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})} \\
- \left(\frac{b_i}{2\sqrt{2} (b_{\mathrm{mix}})^2}\right) \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} + \frac{b_i}{n_{\mathrm{T}} b_{\mathrm{mix}}} \left(\frac{V}{V^2 + 2 n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} \\
+ \frac{1}{2\sqrt{2} n_{\mathrm{T}} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left(\sum_j n_j (a\alpha)_{i,j} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T}\right)\right)
\end{aligned}
\tag{104}
$$

Further simplification yields,

$$
\begin{aligned}
\left.\frac{n_{\mathrm{T}} s_{\mathrm{mix}}}{dn_i}\right|_{V,T,n_j} = s_i^\circ + R \ln\left(\frac{p^\circ (V - n_{\mathrm{T}} b_{\mathrm{mix}})}{n_i RT}\right) - R + \frac{n_{\mathrm{T}} R b_i}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})} \\
- \frac{b_i}{2\sqrt{2} (b_{\mathrm{mix}})^2} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} \\
+ \frac{b_i}{n_{\mathrm{T}} b_{\mathrm{mix}}} \left(\frac{V}{V^2 + 2 n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2}\right) \frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial T} \\
+ \frac{1}{2\sqrt{2} n_{\mathrm{T}} b_{\mathrm{mix}}} \ln\left(\frac{V + (1+\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}{V + (1-\sqrt{2}) n_{\mathrm{T}} b_{\mathrm{mix}}}\right) \left(\sum_j n_j (a\alpha)_{i,j} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T}\right)\right)
\end{aligned}
\tag{105}
$$

Now the other terms in Eq. 100 are calculated as

$$
\left.\frac{d (n_{\mathrm{T}} s_{\mathrm{mix}})}{dp}\right|_{n_i} = -\left.\frac{dV}{dT}\right|_{n_i,P} = \frac{\frac{dP}{dT}_{n_i,V}}{\frac{dP}{dV}_{n_i,V}}
\tag{106}
$$

Hence the partial molar enthalpy is expressed as

$$s_i = \left.\frac{d(n_\mathrm{T} s_\mathrm{mix})}{dn_i}\right|_{p,T,n_j} = \left.\frac{d(n_\mathrm{T} s_\mathrm{mix})}{dn_i}\right|_{V,T,n_j} - \left(\frac{\frac{dP}{dT}_{n_i,V}}{\frac{dP}{dV}_{n_i,V}}\right)\left.\frac{dp}{dn_i}\right|_{V,T,n_j} \tag{107}$$

where

$$\begin{aligned}\left.\frac{n_\mathrm{T} s_\mathrm{mix}}{dn_i}\right|_{V,T,n_j} &= s_i^\circ + R\ln\left(\frac{p^\circ(V-n_\mathrm{T}b_\mathrm{mix})}{n_iRT}\right) - R + \frac{n_\mathrm{T}Rb_i}{(V-n_\mathrm{T}b_\mathrm{mix})}\\ &-\frac{b_i}{2\sqrt{2}(b_\mathrm{mix})^2}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\frac{\partial(n_\mathrm{T}^2a\alpha)_\mathrm{mix}}{\partial T}\\ &+\frac{b_i}{n_\mathrm{T}b_\mathrm{mix}}\left(\frac{V}{V^2+2n_\mathrm{T}b_\mathrm{mix}V-n_\mathrm{T}^2b_\mathrm{mix}^2}\right)\frac{\partial(n_\mathrm{T}^2a\alpha)_\mathrm{mix}}{\partial T}\\ +\frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\ln&\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left(\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}+\frac{1}{\alpha_j}\frac{\partial\alpha_j}{\partial T}\right)\right)\end{aligned} \tag{108}$$

12.4 Partial molar specific heats

Specific heats of individual species can be defined as

$$n_ic_{p,i} = \left.\frac{d(n_ih_i)}{dT}\right|_P = \left.\frac{d(n_ih_i)}{dT}\right|_V - \left.\frac{d(n_ih_i)}{dp}\right|_T\left.\frac{dp}{dT}\right|_V = \left.\frac{d(n_ih_i)}{dT}\right|_V - \left(n_iv_i - T\left.\frac{d(n_iv_i)}{dT}\right|_p\right)\left.\frac{dp}{dT}\right|_V \tag{109}$$

Now

$$\begin{aligned}\left.\frac{d(n_\mathrm{T}h)}{dn_i}\right|_{T,V,n_j} &= h_i^\circ - RT + V\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}b_\mathrm{mix}^2}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\frac{d(a\alpha)_\mathrm{mix}}{dT} - (a\alpha)_\mathrm{mix}\right]\\ &+\frac{n_\mathrm{T}}{b_\mathrm{mix}}\left(\frac{Vb_i}{V^2+2n_\mathrm{T}b_\mathrm{mix}V-n_\mathrm{T}^2b_\mathrm{mix}^2}\right)\left[T\frac{d(n_\mathrm{T}^2a\alpha)_\mathrm{mix}}{dT} - (n_\mathrm{T}^2a\alpha)_\mathrm{mix}\right]\\ +\frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\ln&\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}+\frac{1}{\alpha_j}\frac{\partial\alpha_j}{\partial T}\right) - 2\sum_j n_j(a\alpha)_{ij}\right]\end{aligned} \tag{110}$$

Taking derivative with respect to Temperature,

$$\begin{aligned}\left.\frac{d(h_i)}{dT}\right|_V &= \frac{d(h_i^\circ)}{dT} - R + V\frac{d}{dT}\frac{dp}{dn_i} - \frac{b_i}{2\sqrt{2}b_\mathrm{mix}^2}\ln\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\left[T\frac{d^2(a\alpha)_\mathrm{mix}}{dT^2}\right]\\ &+\frac{n_\mathrm{T}}{b_\mathrm{mix}}\left(\frac{Vb_i}{V^2+2n_\mathrm{T}b_\mathrm{mix}V-n_\mathrm{T}^2b_\mathrm{mix}^2}\right)\left[T\frac{d^2(a\alpha)_\mathrm{mix}}{dT^2}\right]\\ +\frac{1}{2\sqrt{2}n_\mathrm{T}b_\mathrm{mix}}\ln&\left(\frac{V+(1+\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}{V+(1-\sqrt{2})n_\mathrm{T}b_\mathrm{mix}}\right)\frac{d}{dT}\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}+\frac{1}{\alpha_j}\frac{\partial\alpha_j}{\partial T}\right) - 2\sum_j n_j(a\alpha)_{ij}\right].\end{aligned} \tag{111}$$

consider the term

$$\frac{d}{dT}\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}+\frac{1}{\alpha_j}\frac{\partial\alpha_j}{\partial T}\right)-2\sum_j n_j(a\alpha)_{ij}\right]=\frac{d}{dT}\left[2T\sum_j n_j\frac{\partial(a\alpha)_{i,j}}{\partial T}-2\sum_j n_j(a\alpha)_{ij}\right]$$
$$=2\sum_j n_j\frac{\partial(a\alpha)_{i,j}}{\partial T}+2T\sum_j n_j\frac{\partial^2(a\alpha)_{i,j}}{\partial T^2}-2\sum_j n_j\frac{\partial(a\alpha)_{i,j}}{\partial T} \tag{112}$$

Simplification yields,

$$\frac{d}{dT}\left[T\sum_j n_j(a\alpha)_{i,j}\left(\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}+\frac{1}{\alpha_j}\frac{\partial\alpha_j}{\partial T}\right)-2\sum_j n_j(a\alpha)_{ij}\right]=2T\sum_j n_j\frac{\partial^2(a\alpha)_{i,j}}{\partial T^2} \tag{113}$$

Therefore, Eq. 111 can be written as

$$\begin{aligned}\left.\frac{d(h_i)}{dT}\right|_V=\frac{d(h_i^\circ)}{dT}-R+V\frac{d}{dT}\frac{dp}{dn_i}-\frac{b_i}{2\sqrt{2}b_{\mathrm{mix}}^2}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\left[T\frac{d^2(a\alpha)_{\mathrm{mix}}}{dT^2}\right]\\+\frac{n_{\mathrm{T}}}{b_{\mathrm{mix}}}\left(\frac{Vb_i}{V^2+2n_{\mathrm{T}}b_{\mathrm{mix}}V-n_{\mathrm{T}}^2b_{\mathrm{mix}}^2}\right)\left[T\frac{d^2(a\alpha)_{\mathrm{mix}}}{dT^2}\right]\\+\frac{T}{\sqrt{2}n_{\mathrm{T}}b_{\mathrm{mix}}}\ln\left(\frac{V+(1+\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}{V+(1-\sqrt{2})n_{\mathrm{T}}b_{\mathrm{mix}}}\right)\sum_j n_j\frac{\partial^2(a\alpha)_{i,j}}{\partial T^2}.\end{aligned} \tag{114}$$

Consider the term $\frac{d}{dT}\left(\frac{dp}{dn_i}\right)$. Since

$$\begin{aligned}\left.\frac{\partial p}{\partial n_i}\right|_{T,n_j,V}=\frac{RT}{V-n_{\mathrm{T}}b_{\mathrm{mix}}}+\frac{n_{\mathrm{T}}RTb_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2}-\frac{2\sum_j n_j(a\alpha)_{ij}}{V^2+2n_{\mathrm{T}}b_{\mathrm{mix}}V-n_{\mathrm{T}}^2b_{\mathrm{mix}}^2}\\+\frac{2b_in_{\mathrm{T}}^2\,(a\alpha)_{\mathrm{mix}}}{(V^2+2n_{\mathrm{T}}b_{\mathrm{mix}}V-n_{\mathrm{T}}^2b_{\mathrm{mix}}^2)^2}(V-n_{\mathrm{T}}b_{\mathrm{mix}})\end{aligned} \tag{115}$$

$$\begin{aligned}\frac{d}{dT}\left(\frac{dp}{dn_i}\right)=\frac{R}{V-n_{\mathrm{T}}b_{\mathrm{mix}}}+\frac{n_{\mathrm{T}}Rb_i}{(V-n_{\mathrm{T}}b_{\mathrm{mix}})^2}-\frac{2\sum_j n_j\frac{\partial(a\alpha)_{ij}}{\partial T}}{V^2+2n_{\mathrm{T}}b_{\mathrm{mix}}V-n_{\mathrm{T}}^2b_{\mathrm{mix}}^2}\\+\frac{2b_in_{\mathrm{T}}^2}{(V^2+2n_{\mathrm{T}}b_{\mathrm{mix}}V-n_{\mathrm{T}}^2b_{\mathrm{mix}}^2)^2}(V-n_{\mathrm{T}}b_{\mathrm{mix}})\frac{\partial((a\alpha)_{\mathrm{mix}})}{\partial T}\end{aligned} \tag{116}$$

Using above equation, individual specific heat can be calculated using Eq. 114.

References

[1] D.G. Goodwin, R.L. Speth, H.K. Moffat, and B.W. Weber. Cantera: An object-oriented software toolkit for Chemical kinetics, Thermodynamics, and Transport Processes, 2018. Version 2.4.0.

[2] O. Redlich and J.N.S. Kwong. On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chem. Rev.*, 44:233–244, 1949.

[3] D.Y. Peng and D.B. Robinson. A new two-constant equation of state. *Ind. Eng. Chem. Fund.*, 15:59–64, 1976.

[4] M.J. Martinez, C.M. Stone, P.K. Notz, D.Z. Turner, P.L. Hopkins, S. Subia, C. Jove-Colon, H.K. Moffat, J.E. Bean, T. Dewers, K. Klise, J. Red-Horse, R. Field, M. Mesh, S. Davison, H. Yoon, B. Carnes, N. Alger, J. Bishop, and P. Newell. Computational thermal, chemical, fluid, and solid mechanics for geosystems management. Technical report, Sandia National Laboratories, 2011.

[5] K.G. Joback and R.C. Reid. Estimation of pure-component properties from group-contributions. *Chem. Eng. Comm.*, 57:233–243, 1987.

A. Appendix

A.1 Evaluation of volume based P-R EoS

The Peng–Robinson EoS for a pure species is stated as

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \tag{117}$$

$$\begin{gathered}
p(v-b)(v^2+2bv-b^2) = RT(v^2+2bv-b^2) - a\alpha(v-b) \\
(pv-pb)(v^2+2bv-b^2) = RTv^2 + 2bvRT - b^2RT - a\alpha v + a\alpha b \\
pv^3 + 2bpv^2 - pvb^2 - pbv^2 - 2b^2pv + pb^3 = RTv^2 + 2bvRT - b^2RT - a\alpha v + a\alpha b \\
pv^3 + bpv^2 - 3pvb^2 + pb^3 - RTv^2 - 2bvRT + b^2RT + a\alpha v - a\alpha b = 0 \\
pv^3 + (bp - RT)v^2 - (3pb^2 + 2bRT - a\alpha)v + pb^3 + b^2RT - a\alpha b = 0
\end{gathered}$$

Therefore, volume–based P-R Eos can be expressed as

$$v^3 + \left(b - \frac{RT}{p}\right)v^2 + \left(\frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}\right)v + \left(b^3 + b^2\frac{RT}{p} - \frac{a\alpha b}{p}\right) = 0 \tag{118}$$

A.2 Evaluation of species-specific coefficients in P–R EoS

The Peng–Robinson EoS for a pure species is stated as

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \tag{119}$$

Converting to a cubic equation in terms of molar volume (v), we obtain

$$v^3 + \left(b - \frac{RT}{p}\right)v^2 + \left(\frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}\right)v + \left(b^3 + b^2\frac{RT}{p} - \frac{a\alpha b}{p}\right) = 0 \tag{120}$$

The compressibility z for a pure fluid is defined as

$$z = \frac{pv}{RT}, \tag{121}$$

where p, v and T are the pressure, molar volume and temperature respectively. Expressing Eq. 120 in terms of the compressibility z yields

$$\left(\frac{zRT}{p}\right)^3 + \left(b - \frac{RT}{p}\right)\left(\frac{zRT}{p}\right)^2 + \left(\frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}\right)\left(\frac{zRT}{p}\right) + \left(b^3 + b^2\frac{RT}{p} - \frac{a\alpha b}{p}\right) = 0. \tag{122}$$

Further simplification gives a cubic P-R equation represented in terms of compressibility z as

$$z^3 + \left(\frac{pb}{RT} - 1\right)z^2 + \left(\frac{a\alpha p}{R^2T^2} - \frac{3b^2p^2}{R^2T^2} - \frac{2bp}{RT}\right)z + \left(\frac{b^3p^3}{R^3T^3} + \frac{b^2p^2}{R^2T^2} - \frac{a\alpha bp^2}{R^3T^3}\right) = 0. \tag{123}$$

Defining

$$A = \frac{a\alpha p}{R^2T^2}, B = \frac{bp}{RT}, \tag{124}$$

further simplifies the equation as

$$z^3 - (1-B)z^2 + (A - 3B^2 - 2B)z - (AB - B^3 - B^2) = 0. \tag{125}$$

Comparing Eq. 125 with standard cubic form $ax^3 + bx^2 + cx + d = 0$, we have

$$a = 1, b = -(1 - B), c = (A - 3B^2 - 2B), d = -(AB - B^3 - B^2) \tag{126}$$

Typically, the general solution of the cubic involves calculation of few discriminants, given as

$$\Delta_0 = b^2 - 3ac, \Delta = 18abcd - 4b^3d + b^2c^2 - 4ac^3 - 27a^2d^2 = 0 \tag{127}$$

A triple root is obtained for a given cubic, when $\Delta_0 = \Delta_1 = 0$. The cubic P-R EoS has a triple root at the critical point (where vapor and liquid phase coincide). Therefore at the critical point,

$$\Delta_0 = b^2 - 3ac = 0 \tag{128}$$

and

$$\Delta = 18abcd - 4b^3d + b^2c^2 - 4ac^3 - 27a^2d^2 = 0 \tag{129}$$

Substituting $a = 1$ from Eq. 126 in Eq. 128, we get

$$c = \frac{b^2}{3} \tag{130}$$

Substituting Eqs. 126 and 130 in Eq. 129, we get

$$18bd\left(\frac{b^2}{3}\right) - 4b^3d + b^2\left(\frac{b^2}{3}\right)^2 - 4\left(\frac{b^2}{3}\right)^3 - 27d^2 = 0 \tag{131}$$

Simplification yields,

$$54b^3d - b^6 - 729d^2 = (27d - b^3)^2 = 0 \tag{132}$$

Therefore,

$$27d = b^3 \tag{133}$$

Now substituting Eq. 126 in Eq. 133, we obtain

$$-27(AB - B^3 - B^2) = -(1 - B)^3 \tag{134}$$

$$27AB - 27B^3 - 27B^2 = 1 - 3B + 3B^2 - B^3 \tag{135}$$

$$26B^3 + 30B^2 - 3B(1 + 9A) + 1 = 0 \tag{136}$$

substituting Eq. 126 in Eq. 130, we get

$$(1 - B)^2 = 3(A - 3B^2 - 2B) \tag{137}$$

$$1 + B^2 - 2B = 3A - 9B^2 - 6B \tag{138}$$

$$1 + 10B^2 + 4B = 3A \tag{139}$$

Hence

$$A = \frac{1 + 10B^2 + 4B}{3} \tag{140}$$

Substituting Eq. 140 in Eq. 136,

$$26B^3 + 30B^2 - 3B(1 + 3(1 + 10B^2 + 4B)) + 1 = 0 \tag{141}$$

$$26B^3 + 30B^2 - 3B(4 + 30B^2 + 12B) + 1 = 0 \tag{142}$$

$$26B^3 + 30B^2 - 12B - 90B^3 - 36B^2 + 1 = 0 \tag{143}$$

$$-64B^3 - 6B^2 - 12B + 1 = 0 \tag{144}$$

$$64B^3 + 6B^2 + 12B - 1 = 0 \tag{145}$$

The solution of Eq. 145 can be calculated using regular cubic equation solver.
Let

$$p = 64, q = 6, r = 12, s = -1 \tag{146}$$

$$\Delta = 18pqrs - 4q^3s + q^2r^2 - 4pr^3 - 27p^2s^2 \tag{147}$$

$$\Delta = -629856 = -2^5 3^9 \tag{148}$$

Since $\Delta \leq 0$, the equation has only one real root.

$$\Delta^\circ = q^2 - 3pr = 36 - 12 \times 3 \times 64 = -2^2 \times 3^4 \times 7 \tag{149}$$

$$\Delta^1 = 2q^3 - 9pqr + 27p^2s = 2 \times 6^3 - 9 \times 72 \times 64 - 27 \times 64^2 = -151632 = -2^4 \times 3^6 \times 13 \tag{150}$$

Let

$$C^\circ = \left[\frac{\Delta^1 \pm \sqrt{(\Delta^1)^2 - 4(\Delta^\circ)^3}}{2}\right]^{1/3} = \left[\frac{\Delta^1 \pm \sqrt{-27p^2\Delta}}{2}\right]^{1/3} \tag{151}$$

$$C^\circ = \left[\frac{-2^4 \times 3^6 \times 13 \pm \sqrt{3^{12}2^{17}}}{2}\right]^{1/3} \tag{152}$$

$$C^\circ = \left[\frac{-2^4 \times 3^6 \times 13 \pm 3^6 2^8 \sqrt{2}}{2}\right]^{1/3} \tag{153}$$

$$C^\circ = \left[2^3 3^6 (-13 \pm 16\sqrt{2})\right]^{1/3} \tag{154}$$

$$C^\circ = 2^1 3^2 \left[-13 \pm 16\sqrt{2}\right]^{1/3} \tag{155}$$

Using these values , root of Eq. 145 is given as

$$B = -\frac{1}{3p}\left(q + C^\circ + \frac{\Delta^\circ}{C^\circ}\right) \tag{156}$$

$$B = -\frac{1}{2^6 3^1}\left(2 \times 3 + 2^1 3^2 \left[-13 \pm 16\sqrt{2}\right]^{1/3} - \frac{2^2 \times 3^4 \times 7}{2^1 3^2 \left[-13 \pm 16\sqrt{2}\right]^{1/3}}\right) \tag{157}$$

Note that

$$\left[-13 + 16\sqrt{2}\right]^{1/3}\left[-13 - 16\sqrt{2}\right]^{1/3} = (169 - 512)^{1/3} = 343^{1/3} = -7 \tag{158}$$

Hence, multiplying and dividing the last term by the conjugate, we obtain

$$B = -\frac{1}{2^5}\left(1 + 3\left[-13 \pm 16\sqrt{2}\right]^{1/3} - \frac{3 \times 7 \left[-13 \mp 16\sqrt{2}\right]^{1/3}}{-7}\right) \tag{159}$$

$$B = -\frac{1}{2^5}\left(1 + 3\left[-13 \pm 16\sqrt{2}\right]^{1/3} + 3\left[-13 \mp 16\sqrt{2}\right]^{1/3}\right) \tag{160}$$

Solution of above equation gives one real root and two imaginary roots. Since, we are only interested in the real root,

$$B = -\frac{1}{2^5}\left(1 + 3\left[-13 + 16\sqrt{2}\right]^{1/3} + 3\left[-13 - 16\sqrt{2}\right]^{1/3}\right) = 0.0777960739038885 \tag{161}$$

From Eq. 140,

$$A = \frac{1 + 10B^2 + 4B}{3} = 0.45723552892138218 \tag{162}$$

These values of A and B are obtained at the triple root point, which in turn is the critical point of the gas. Substituting Eq. 2 in Eq. 124,

$$B = \frac{bp_c}{RT_c} = \left(\frac{b_0 RT_c}{p_c}\right)\frac{p_c}{RT_c} = b_0 = 0.0777960739038885 \tag{163}$$

and

$$A = \frac{a\alpha_c p_c}{R^2T_c^2} = \left(\frac{a_0 R^2 T_c^2}{p_c}\right)\frac{\alpha_c p_c}{R^2T_c^2} = a_0 \tag{164}$$

Note here, $\alpha_c = 1$. To summarize, the coefficients in P–R equation are obtained as

$$b_0 = 0.0777960739038885, a_0 = 0.45723552892138218 \tag{165}$$

Finally, the critical compressibility is calculated by finding the root of Eq. 125.

$$z_c = -\frac{b}{3a} = -\frac{(B-1)}{3} = 0.307401308698703833 \tag{166}$$

A.3 Nickalls Method

The solution for the cubic Peng-Robinson equation(Eq. 125) is obtained using an approach described by Nickalls [5]. The present section describes this methodology and applies it to the cubic Peng-Robinson equation of state.
Consider a generized form of a cubic equation

$$p_0v^3 + q_0v^2 + r_0v + s_0 = 0. \tag{167}$$

The center of the cubic is given as

$$x_N = -\frac{q_0}{3p_0}. \tag{168}$$

The depressed form of Eq. 167 is obtained by substituting ($v = z + x_N$) in the equation. Therefore, we obtain

$$z^3 - 3\delta^2 z + \frac{y_N}{p_0} = 0, \tag{169}$$

where,

$$\delta^2 = \frac{q_0^2 - 3p_0r_0}{9p_0^2}, y_N = \frac{2p_0q_0^3 - 9p_0^2q_0r_0 + 27p_0^3s_0}{27p_0^3} \tag{170}$$

Assuming (α, β, γ) to be roots of Eq. 167, the roots of Eq. 169 are $(z_1 = \alpha - x_N, z_2 = \beta - x_N, z_3 = \gamma - x_N)$. Comparing the cubic Eq. 169 with a standard identity $(m+n)^3 - 3mn(m+n) - (m^3+n^3) = 0$, we have

$$(m+n) = z, mn = \delta^2, m^3 + n^3 = -\frac{y_N}{p_0} \tag{171}$$

Solving above equations by taking the cube of the m term and substituting for n,

$$m^6 + \frac{y_N}{p_0}m^3 + \delta^6 = 0 \tag{172}$$

Solving above quadratic equation in m^3, we obtain

$$m^3 = \frac{-y_N \pm \sqrt{y_N^2 - 4\delta^6 p_0^2}}{2p_0} \tag{173}$$

Let

$$h^2 = 4p^2\delta^6, y_{\mathrm{N}} + h = y_{\mathrm{T1}}, y_{\mathrm{N}} - h = y_{\mathrm{T2}} \tag{174}$$

$$\Delta_3 = y_{\mathrm{T1}} y_{\mathrm{T2}} = y_{\mathrm{N}}^2 - h^2 \tag{175}$$

Hence

$$m^3 = \frac{-y_{\mathrm{N}} \pm \sqrt{y_{\mathrm{T1}} y_{\mathrm{T2}}}}{2p_0} = \frac{-y_{\mathrm{N}} \pm \sqrt{\Delta_3}}{2p_0}. \tag{176}$$

Also

$$n^3 = \left[\frac{-y_{\mathrm{N}}}{p_0} - m^3\right] = -\frac{y_{\mathrm{N}}}{p_0} - \frac{-y_{\mathrm{N}} \pm \sqrt{\Delta_3}}{2p_0} = \frac{-y_{\mathrm{N}} \mp \sqrt{\Delta_3}}{2p_0}. \tag{177}$$

It is clear from Eqs. 176 and 177 that the value and sign of the discriminant Δ_3 dictates number of real and complex roots.

A.3.1 Case 1: $y_{\mathbf{N}}^2 > h^2$ i.e. $y_{\mathbf{T1}} y_{\mathbf{T2}} > 0$

With $\Delta_3 > 0$, Eqs. 176 and 177 yield

$$z = m + n = \left[\frac{-y_{\mathrm{N}} + \sqrt{\Delta_3}}{2p_0}\right]^{1/3} + \left[\frac{-y_{\mathrm{N}} - \sqrt{\Delta_3}}{2p_0}\right]^{1/3}. \tag{178}$$

Thus we have only one real root for Eq. 167 in this case, which is given by:

$$\alpha = x_{\mathrm{N}} + \left[\frac{-y_{\mathrm{N}} + \sqrt{\Delta_3}}{2p}\right]^{1/3} + \left[\frac{-y_{\mathrm{N}} - \sqrt{\Delta_3}}{2p}\right]^{1/3}. \tag{179}$$

A.3.2 Case 2: $y_{\mathbf{N}}^2 = h^2$ i.e. $y_{\mathbf{T1}} y_{\mathbf{T2}} = 0$

With $\Delta_3 = 0$, Eqs. 176 and 177 reduce to

$$m = n = \left[\frac{-y_{\mathrm{N}}}{2p}\right]^{1/3}. \tag{180}$$

Since $\delta^2 = mn$,

$$\delta = \pm\left[\frac{-y_{\mathrm{N}}}{2p}\right]^{1/3}. \tag{181}$$

The roots for Eq. 169 are

$$z_1 = -2\delta, z_2 = \delta, z_3 = \delta. \tag{182}$$

and roots of Eq. 167 are

$$\alpha = x_{\mathrm{N}} - 2\delta, \beta = x_{\mathrm{N}} + \delta, \gamma = x_{\mathrm{N}} + \delta. \tag{183}$$

Furthermore, if $y_{\mathrm{N}} = h = 0$, then

$$\delta = 0 \tag{184}$$

In this case, three equal roots are obtained as

$$\alpha = \beta = \gamma = x_{\mathrm{N}}. \tag{185}$$

A.3.3 Case 3: $y_{\mathbf{N}}^2 < h^2$ i.e. $y_{\mathbf{T1}} y_{\mathbf{T2}} < 0$

With $\Delta_3 < 0$, three distinct roots are obtained. Assuming $z = 2\delta\cos\theta$, Eq. 169 becomes

$$8\delta^3(\cos\theta)^3 - 6\delta^3\cos\theta + \frac{y_{\mathrm{N}}}{p_0} = 0 \tag{186}$$

Using Eq.174,

$$4h(\cos\theta)^3 - 3h\cos\theta + y_{\mathrm{N}} = 0 \tag{187}$$

Above equation further simplifies to

$$\cos(3\theta) = 4(\cos\theta)^3 - 3\cos\theta = -\frac{y_{\mathrm{N}}}{h}\text{i.e.}y_{\mathrm{N}} = -h\cos(3\theta) \tag{188}$$

the above identity implies

$$\Delta_3 = -h^2\sin^2(3\theta) \tag{189}$$

The roots of Eq. 169 can be obtained as

$$z = \left[\frac{h}{2p_0}(\cos3\theta + i\sin3\theta)\right]^{1/3} + \left[\frac{h}{2p_0}(\cos3\theta - i\sin3\theta)\right]^{1/3} = \delta\left[(\cos\theta + i\sin\theta) + (\cos\theta - i\sin\theta)\right] \tag{190}$$

where i is the imaginary number $\sqrt{-1}$. Therefore, three roots for Eq. 169 are

$$z_1 = 2\delta\cos\theta, z_2 = 2\delta\cos(\theta + 2\pi/3), z_3 = 2\delta\cos(\theta + 4\pi/3) \tag{191}$$

Hence three roots for Eq. 167 are

$$\alpha = x_{\mathrm{N}} + 2\delta\cos\theta \tag{192}$$

$$\beta = x_{\mathrm{N}} + 2\delta\cos\left(\theta + \frac{2\pi}{3}\right) \tag{193}$$

$$\gamma = x_{\mathrm{N}} + 2\delta\cos\left(\theta + \frac{4\pi}{3}\right) \tag{194}$$

A.4 Solution to cubic P-R EoS

The volume based P–R equation is stated as

$$v^3 + \left(b - \frac{RT}{p}\right)v^2 + \left(\frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}\right)v + \left(b^3 + b^2\frac{RT}{p} - \frac{a\alpha b}{p}\right) = 0 \tag{195}$$

Comparing Eqs. 167 and 195, the coefficients of the cubic are expressed as

$$p_0 = 1, q_0 = b - \frac{RT}{p}, r_0 = \frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}, s_0 = b^3 + b^2\frac{RT}{p} - \frac{a\alpha b}{p} \tag{196}$$

Substituting these values in Eq. 167, the depressed cubic equation is obtained as

$$y^3 - 3\delta^2 y + y_{\mathrm{N}} = 0 \tag{197}$$

where,

$$9\delta^2 = \left(b - \frac{RT}{p}\right)^2 - 3\left(\frac{a\alpha}{p} - 3b^2 - 2b\frac{RT}{p}\right) \tag{198}$$

and

$$y_{\mathrm{N}} = \frac{2q_0^3 - 9q_0r_0 + 27s_0}{27} \tag{199}$$

The roots for molar volume v can be obtained using the analysis explained in Sec. A.3.

A.5 Required derivatives of P–R coefficients

A.5.1 Derivative of α with respect to temperature

$$\alpha_i = \left[1 + \kappa_i \left(1 - \sqrt{T_r}\right)\right]^2 \tag{200}$$

where

$$T_r = \frac{T}{T_{\mathrm{c}}} \quad \text{and} \quad \frac{\partial(\mathrm{T_r})}{\partial \mathrm{T}} = \frac{1}{\mathrm{T_c}} \tag{201}$$

Taking derivative of above equation with respect to temperature yields,

$$\frac{\partial \alpha_i}{\partial T} = \frac{\partial}{\partial T}\left[1 + \kappa_i^2 \left(1 - 2\sqrt{T_r} + T_r\right) + 2\kappa_i(1 - \sqrt{T_r})\right] \tag{202}$$

$$\frac{\partial \alpha_i}{\partial T} = \kappa_i^2 \left(-\frac{1}{T_{\mathrm{c}}\sqrt{T_r}} + \frac{1}{T_{\mathrm{c}}}\right) - \kappa_i \frac{1}{\sqrt{T_r}T_{\mathrm{c}}} \tag{203}$$

$$\frac{\partial \alpha_i}{\partial T} = \frac{1}{T_{\mathrm{c}}\sqrt{T_r}}\left[\kappa_i^2 \left(\sqrt{T_r} - 1\right) - \kappa_i\right] \tag{204}$$

Second derivative:

$$\frac{\partial^2 \alpha_i}{\partial T^2} = \frac{-1}{2T_{\mathrm{c}}^2 T_r \sqrt{T_r}}\left[\kappa_i^2 \left(\sqrt{T_r} - 1\right) - \kappa_i\right] + \frac{1}{T_{\mathrm{c}}\sqrt{T_r}}\left[\kappa_i^2 \frac{1}{2\sqrt{T_r}T_{\mathrm{c}}}\right] \tag{205}$$

$$\frac{\partial^2 \alpha_i}{\partial T^2} = \frac{-1}{2T_{\mathrm{c}}^2 T_r \sqrt{T_r}}\left[\kappa_i^2 \left(\sqrt{T_r} - 1\right) - \kappa_i\right] + \frac{\kappa_i^2}{2T_{\mathrm{c}}^2 T_r} \tag{206}$$

$$\frac{\partial^2 \alpha_i}{\partial T^2} = \frac{\kappa_i^2 + \kappa_i}{2T_{\mathrm{c}}^2 T_r \sqrt{T_r}} \tag{207}$$

A.5.2 Derivatives of $a\alpha_{i,j}$ with respect to temperature

$$\frac{\partial(a\alpha_{i,j})}{\partial T} = \frac{\partial}{\partial T}\sqrt{(a\alpha)_i (a\alpha_j)} \tag{208}$$

Taking derivative, we get

$$\frac{\partial(a\alpha_{i,j})}{\partial T} = \frac{1}{2}\sqrt{\frac{(a\alpha)_j}{(a\alpha)_i}}\frac{\partial}{\partial T}(a\alpha)_i + \frac{1}{2}\sqrt{\frac{(a\alpha)_i}{(a\alpha)_j}}\frac{\partial}{\partial T}(a\alpha)_j \tag{209}$$

Simplification yields,

$$\frac{\partial(a\alpha_{i,j})}{\partial T} = \frac{1}{2}\sqrt{(a\alpha)_i (a\alpha_j)}\left[\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right] = 0.5(a\alpha)_{i,j}\left[\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right] \tag{210}$$

Now taking second derivative with respect to the temperature, we obtain

$$\frac{\partial^2(a\alpha_{i,j})}{\partial T^2} = \frac{1}{2}\frac{\partial(a\alpha_{i,j})}{\partial T}\left[\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right] + \frac{(a\alpha)_{i,j}}{2}\left[-\frac{1}{\alpha_i^2}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_i}\frac{\partial^2 \alpha_i}{\partial T^2} - \frac{1}{\alpha_j^2}\frac{\partial \alpha_j}{\partial T} + \frac{1}{\alpha_j}\frac{\partial^2 \alpha_j}{\partial T^2}\right] \tag{211}$$

$$\frac{\partial^2(a\alpha_{i,j})}{\partial T^2} = \frac{a\alpha_{i,j}}{4}\left[\frac{1}{\alpha_i}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j}\frac{\partial \alpha_j}{\partial T}\right]^2 + \frac{(a\alpha)_{i,j}}{2}\left[-\frac{1}{\alpha_i^2}\frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_i}\frac{\partial^2 \alpha_i}{\partial T^2} - \frac{1}{\alpha_j^2}\frac{\partial \alpha_j}{\partial T} + \frac{1}{\alpha_j}\frac{\partial^2 \alpha_j}{\partial T^2}\right] \tag{212}$$

A.5.3 Derivative of $\alpha_{\mathbf{mix}}$ with respect to temperature

For multi-component mixture,

$$(a\alpha)_{\text{mix}} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} = \sum_i \sum_j X_i X_j \sqrt{(a\alpha)_i (a\alpha)_j} \tag{213}$$

Hence

$$\frac{\partial (a\alpha)_{\text{mix}}}{\partial T} = \sum_i \sum_j X_i X_j \sqrt{a_i a_j} \frac{\partial \sqrt{(\alpha)_i (\alpha)_j}}{\partial T} \tag{214}$$

$$\frac{\partial (a\alpha)_{\text{mix}}}{\partial T} = \sum_i \sum_j X_i X_j \frac{\sqrt{a_i a_j}}{2\sqrt{\alpha_i \alpha_j}} \left(\alpha_j \frac{\partial \alpha_i}{\partial T} + \alpha_i \frac{\partial \alpha_j}{\partial T} \right) \tag{215}$$

$$\frac{\partial (a\alpha)_{\text{mix}}}{\partial T} = \sum_i \sum_j \frac{X_i X_j \sqrt{a_i a_j}}{2\sqrt{\alpha_i \alpha_j}} \left(\alpha_j \frac{\partial \alpha_i}{\partial T} + \alpha_i \frac{\partial \alpha_j}{\partial T} \right) \tag{216}$$

Second derivative with respect to T is

$$\frac{\partial^2 (a\alpha)_{\text{mix}}}{\partial T^2} = \sum_i \sum_j \frac{X_i X_j \sqrt{a_i a_j}}{2} \left[-\frac{1}{2(\alpha_i \alpha_j)^{3/2}} \left(\alpha_j \frac{\partial \alpha_i}{\partial T} + \alpha_i \frac{\partial \alpha_j}{\partial T} \right)^2 + \frac{1}{\sqrt{\alpha_i \alpha_j}} \left(\alpha_j \frac{\partial^2 \alpha_i}{\partial T^2} + \alpha_i \frac{\partial^2 \alpha_j}{\partial T^2} + 2 \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} \right) \right] \tag{217}$$

$$\frac{\partial^2 (a\alpha)_{\text{mix}}}{\partial T^2} = \sum_i \sum_j \frac{X_i X_j \sqrt{a_i a_j}}{2\sqrt{\alpha_i \alpha_j}} \left[-\frac{1}{2(\alpha_i \alpha_j)} \left(\alpha_j \frac{\partial \alpha_i}{\partial T} + \alpha_i \frac{\partial \alpha_j}{\partial T} \right)^2 + \left(\alpha_j \frac{\partial^2 \alpha_i}{\partial T^2} + \alpha_i \frac{\partial^2 \alpha_j}{\partial T^2} + 2 \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} \right) \right] \tag{218}$$

Further simplifying, we obtain

$$\frac{\partial^2 (a\alpha)_{\text{mix}}}{\partial T^2} = \sum_i \sum_j \frac{X_i X_j (a\alpha)_{i,j}}{2\alpha_i \alpha_j} \left[-\frac{1}{2(\alpha_i \alpha_j)} \left(\alpha_j \frac{\partial \alpha_i}{\partial T} + \alpha_i \frac{\partial \alpha_j}{\partial T} \right)^2 + \left(\alpha_j \frac{\partial^2 \alpha_i}{\partial T^2} + \alpha_i \frac{\partial^2 \alpha_j}{\partial T^2} + 2 \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} \right) \right] \tag{219}$$

$$\frac{\partial^2 (a\alpha)_{\text{mix}}}{\partial T^2} = \sum_i \sum_j \frac{X_i X_j (a\alpha)_{i,j}}{2\alpha_i \alpha_j} \left[-\frac{(\alpha_i \alpha_j)}{2} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T} \right)^2 + \left(\alpha_j \frac{\partial^2 \alpha_i}{\partial T^2} + \alpha_i \frac{\partial^2 \alpha_j}{\partial T^2} + 2 \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} \right) \right] \tag{220}$$

$$\frac{\partial^2 (a\alpha)_{\text{mix}}}{\partial T^2} = \sum_i \sum_j \frac{X_i X_j (a\alpha)_{i,j}}{2} \left[-\frac{1}{2} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} + \frac{1}{\alpha_j} \frac{\partial \alpha_j}{\partial T} \right)^2 + \left(\frac{1}{\alpha_i} \frac{\partial^2 \alpha_i}{\partial T^2} + \frac{1}{\alpha_j} \frac{\partial^2 \alpha_j}{\partial T^2} + \frac{2}{\alpha_i \alpha_j} \frac{\partial \alpha_i}{\partial T} \frac{\partial \alpha_j}{\partial T} \right) \right] \tag{221}$$

A.5.4 Derivatives of a,b with respect to number of moles

$$(a\alpha)_{\text{mix}} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} = \sum_i \sum_j X_i X_j \sqrt{(a\alpha)_i (a\alpha)_j} \tag{222}$$

Hence

$$\frac{\partial (n_{\text{T}}^2 a\alpha)_{\text{mix}}}{\partial n_k} = \frac{\partial}{\partial n_k} \left(\sum_i \sum_j n_i n_j (a\alpha)_{ij} \right) \tag{223}$$

$$\frac{\partial (n_{\text{T}}^2 a\alpha)_{\text{mix}}}{\partial n_k} = \sum_{i \neq k} n_i \frac{\partial}{\partial n_k} \left(\sum_j n_j (a\alpha)_{ij} \right) + \frac{\partial}{\partial n_k} \left(n_k \sum_j n_j (a\alpha)_{kj} \right) \tag{224}$$

Simplifying,

$$\frac{\partial (n_{\mathrm{T}}^2 a\alpha)_{\mathrm{mix}}}{\partial n_k} = \sum_{i\neq k} n_i (a\alpha)_{ik} + \sum_j n_j (a\alpha)_{kj} + n_k (a\alpha)_{kk} = 2\sum_j n_j (a\alpha)_{kj} \tag{225}$$

$$b_{\mathrm{mix}} = \sum_i \frac{n_i}{n_{\mathrm{T}}} b_i \tag{226}$$

Hence

$$\frac{\partial (n_{\mathrm{T}} b_{\mathrm{mix}})}{\partial n_i} = b_i \tag{227}$$

A.6 Pressure Derivatives

Multicomponent P–R EoS is given by:

$$p = \frac{RT}{v - b_{\mathrm{mix}}} - \frac{(a\alpha)_{\mathrm{mix}}}{v^2 + 2b_{\mathrm{mix}} v - b_{\mathrm{mix}}^2} \tag{228}$$

In terms of total volume V,

$$p = \frac{n_{\mathrm{T}} RT}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} - \frac{n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2} \tag{229}$$

A.6.1 Pressure derivative with respect to Temperature

$$\left.\frac{\partial p}{\partial T}\right|_{V,n_i} = \frac{n_{\mathrm{T}} R}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} - \frac{n_{\mathrm{T}}^2}{V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2} \left(\frac{\partial (a\alpha)_{\mathrm{mix}}}{\partial T}\right) \tag{230}$$

Note here a and b are temperature independent. We only need derivative of $(a\alpha)_{\mathrm{mix}}$ with respect to temperature, which is given by Eq. 216.

A.6.2 Pressure derivative with respect to volume

$$\left.\frac{\partial p}{\partial V}\right|_{T,n_{\mathrm{T}}} = -\frac{n_{\mathrm{T}} RT}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})^2} + \frac{n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{(V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2)^2} (2V + 2n_{\mathrm{T}} b_{\mathrm{mix}}) \tag{231}$$

$$\left.\frac{\partial p}{\partial V}\right|_{T,n_{\mathrm{T}}} = -\frac{n_{\mathrm{T}} RT}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})^2} + \frac{2n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{(V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2)^2} (V + n_{\mathrm{T}} b_{\mathrm{mix}}) \tag{232}$$

A.6.3 Pressure derivative with respect to number of moles

$$p = \frac{n_{\mathrm{T}} RT}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} - \frac{n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2} \tag{233}$$

$$\begin{aligned}\left.\frac{\partial p}{\partial n_i}\right|_{T,n_j,V} = {} & \frac{RT}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}} RT b_i}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})^2} - \frac{2\sum_j n_j (a\alpha)_{ij}}{V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2} \\ & + \frac{n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{(V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2)^2} (2b_i V - 2n_{\mathrm{T}} b_{\mathrm{mix}} b_i)\end{aligned} \tag{234}$$

$$\begin{aligned}\left.\frac{\partial p}{\partial n_i}\right|_{T,n_j,V} = {} & \frac{RT}{V - n_{\mathrm{T}} b_{\mathrm{mix}}} + \frac{n_{\mathrm{T}} RT b_i}{(V - n_{\mathrm{T}} b_{\mathrm{mix}})^2} - \frac{2\sum_j n_j (a\alpha)_{ij}}{V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2} \\ & + \frac{2b_i n_{\mathrm{T}}^2 (a\alpha)_{\mathrm{mix}}}{(V^2 + 2n_{\mathrm{T}} b_{\mathrm{mix}} V - n_{\mathrm{T}}^2 b_{\mathrm{mix}}^2)^2} (V - n_{\mathrm{T}} b_{\mathrm{mix}})\end{aligned} \tag{235}$$