

Implementation of Multi-component Soave-Redlich-Kwong Equation of State in Cantera

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1 Overview

In addition to the ideal gas equation of state (EoS), CANTERA [1] currently has implementations of the Redlich-Kwong [3] and Peng-Robinson [2] real gas equations of state. This paper outlines the approach taken to implement the Soave modification [4] of the Redlich-Kwong EoS.

2 Soave-Redlich-Kwong EoS

The Soave-Redlich-Kwong (SRK) EoS is given by

$$p = \frac{RT}{\nu - b} - \frac{a\alpha}{\nu(\nu + b)} \quad (1)$$

where p is pressure, R is the universal gas constant, T is temperature, and ν is the molar volume. The species-specific Van der Waals attraction parameter a and the repulsive, volume correction parameter b are calculated as

$$a = \frac{\Omega_a R^2 T_c^2}{p_c} \quad (2)$$

$$b = \frac{\Omega_b R T_c}{p_c} \quad (3)$$

where the constants Ω_a and Ω_b are defined as

$$\Omega_a = \left[9(2^{1/3} - 1) \right]^{-1} \approx 0.42748 \quad (4)$$

$$\Omega_b = \frac{2^{1/3} - 1}{3} \approx 0.08664 \quad (5)$$

The temperature dependent interaction parameter α is given as

$$\alpha(T) = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (6)$$

where κ is given by

$$\kappa = 0.480 + 1.574\omega - 0.176\omega^2 \quad (7)$$

which is a function of the acentric factor (ω) of the species.

2.1 Multi-component Soave-Redlich-Kwong EoS

The pure fluid SRK EoS can be generalized for a multi-component mixture as

$$p = \frac{RT}{\nu - b_{mix}} - \frac{(a\alpha)_{mix}}{\nu(\nu + b_{mix})} \quad (8)$$

The mixture averaged properties are defined as

$$a_{mix} = \sum_i \sum_j X_i X_j a_{ij} \quad (9)$$

$$b_{mix} = \sum_i X_i b_i \quad (10)$$

$$(a\alpha)_{mix} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} \quad (11)$$

The default species interaction parameters a_{ij} and $(a\alpha)_{ij}$ are defined by the geometric average of the pure-species parameters

$$a_{ij} = \sqrt{a_i a_j} \quad (12)$$

$$(a\alpha)_{ij} = \sqrt{(a\alpha)_i (a\alpha)_j} \quad (13)$$

2.2 Critical properties

Critical properties can be calculated from the species parameters, a and b , and the EoS-specific constants. Dividing (2) by (3) gives

$$\frac{a}{b} = \frac{\Omega_a R T_c}{\Omega_b}$$

solving for critical temperature yields

$$T_c = \frac{a \Omega_b}{b \Omega_a R} \quad (14)$$

Rearranging (3) to solve for critical pressure

$$p_c = \frac{\Omega_b R T_c}{b}$$

and then substituting (14) yields

$$p_c = \frac{a\Omega_b^2}{\Omega_a b^2} \quad (15)$$

The critical properties for the multi-component case can also be calculated from the mixture averaged properties using

$$T_{c,mix} = \frac{a_{mix}\Omega_b}{b_{mix}\Omega_a R} \quad (16)$$

$$p_{c,mix} = \frac{a_{mix}\Omega_b^2}{\Omega_a b_{mix}^2} \quad (17)$$

2.3 Cubic Form

The cubic form in terms of molar volume can be obtained by multiplying both sides of (1) by the denominators of the right hand side which gives

$$p\nu(\nu - b)(\nu + b) = RT\nu(\nu + b) - a\alpha(\nu - b)$$

expanding and rearranging gives

$$\begin{aligned} p\nu(\nu^2 - b^2) &= RT(\nu^2 + b\nu) - a\alpha(\nu - b) \\ p\nu^3 - b^2p\nu - RT\nu^2 - bRT\nu + a\alpha\nu - a\alpha b &= 0 \end{aligned}$$

finally, grouping like terms and dividing by pressure yields the cubic form

$$\nu^3 - \frac{RT}{p}\nu^2 + \left(\frac{a\alpha - bRT}{p} - b^2\right)\nu - \frac{a\alpha b}{p} = 0 \quad (18)$$

The cubic form can also be written in terms of the compressibility factor (Z) which is defined as

$$Z = \frac{P\nu}{RT} \quad (19)$$

Therefore, substituting the corresponding definition of molar volume in terms of compressibility factor

$$\nu = \frac{ZRT}{P} \quad (20)$$

into (18) gives

$$\left(\frac{RT}{P}\right)^3 Z^3 - \left(\frac{RT}{P}\right)^3 Z^2 + \frac{RT}{p} \left(\frac{a\alpha - bRT}{p} - b^2\right) Z - \frac{a\alpha b}{p} = 0$$

dividing through by the first coefficient yields

$$Z^3 - Z^2 + \left[\frac{a\alpha p}{R^2 T^2} - \frac{bp}{RT} - \left(\frac{bp}{RT}\right)^2\right] Z - \frac{a\alpha bp^2}{R^3 T^3} = 0$$

which can finally be written as

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (21)$$

where the terms are A and B are given by

$$A = \frac{a\alpha p}{R^2 T^2} \quad (22)$$

$$B = \frac{bp}{RT} \quad (23)$$

or for the multi-component SRK

$$A_{mix} = \frac{(a\alpha)_{mix} p}{R^2 T^2} \quad (24)$$

$$B_{mix} = \frac{b_{mix} p}{RT} \quad (25)$$

3 Derivatives

3.1 Pressure

The pressure derivatives of the multi-component SRK equation of state (8) with respect to ν and T are given by

$$\left(\frac{\partial p}{\partial \nu}\right)_T = -\frac{RT}{(\nu - b_{mix})^2} + (a\alpha)_{mix} \frac{2\nu + b_{mix}}{[\nu(\nu + b_{mix})]^2} \quad (26)$$

$$\left(\frac{\partial p}{\partial T}\right)_\nu = \frac{R}{\nu - b_{mix}} - \frac{1}{\nu(\nu + b_{mix})} \frac{\partial(a\alpha)_{mix}}{\partial T} \quad (27)$$

3.2 Molar volume

3.2.1 Isothermal Compressibility

Isothermal compressibility is defined as

$$\beta_T = -\frac{1}{\nu} \left(\frac{\partial \nu}{\partial p}\right)_T \quad (28)$$

Since the inverse of this derivative is much more easily calculated, we can apply the inverse function theorem under the assumption that the Jacobian determinant is nonzero

$$\left(\frac{\partial \nu}{\partial p}\right)_T = \left(\frac{\partial p}{\partial \nu}\right)_T^{-1}$$

Therefore, the isothermal compressibility takes the final form

$$\beta_T = -\left[\nu \left(\frac{\partial p}{\partial \nu}\right)_T\right]^{-1} \quad (29)$$

from the derivative of pressure with respect to molar volume (26).

3.2.2 Thermal Expansion Coefficient

The volumetric thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_p \quad (30)$$

Applying the triple product rule

$$\left(\frac{\partial \nu}{\partial T} \right)_p \left(\frac{\partial p}{\partial \nu} \right)_T \left(\frac{\partial T}{\partial p} \right)_\nu = -1$$

Once again applying the inverse function theorem, and then solving for the derivative of molar volume with respect to temperature yields

$$\left(\frac{\partial \nu}{\partial T} \right)_p = - \frac{\left(\frac{\partial p}{\partial T} \right)_\nu}{\left(\frac{\partial p}{\partial \nu} \right)_T}$$

Therefore, the thermal expansion coefficient takes the final form

$$\alpha_V = - \frac{1}{\nu} \frac{\left(\frac{\partial p}{\partial T} \right)_\nu}{\left(\frac{\partial p}{\partial \nu} \right)_T} \quad (31)$$

from the derivatives of pressure with respect to temperature (27) and molar volume (26).

3.3 Mixing Expressions

Of the mixture averaged parameters, only $(a\alpha)_{mix}$ is temperature-dependent. The derivative of (11) with respect to temperature is simply the sum of the derivatives of all of the species interaction parameters

$$\frac{\partial(a\alpha)_{mix}}{\partial T} = \sum_i \sum_j X_i X_j \frac{\partial(a\alpha)_{ij}}{\partial T} \quad (32)$$

Therefore, taking the derivative of (13) with respect to temperature

$$\frac{\partial(a\alpha)_{ij}}{\partial T} = \frac{1}{2\sqrt{(a\alpha)_i(a\alpha)_j}} \left[\frac{\partial(a\alpha)_i}{\partial T} (a\alpha)_j + (a\alpha)_i \frac{\partial(a\alpha)_j}{\partial T} \right]$$

which can be written

$$\frac{\partial(a\alpha)_{ij}}{\partial T} = \frac{\sqrt{(a\alpha)_i(a\alpha)_j}}{2} \left[\frac{1}{(a\alpha)_i} \frac{\partial(a\alpha)_i}{\partial T} + \frac{1}{(a\alpha)_j} \frac{\partial(a\alpha)_j}{\partial T} \right]$$

and after substituting (13) yields

$$\frac{\partial(a\alpha)_{ij}}{\partial T} = \frac{(a\alpha)_{ij}}{2} \left[\frac{1}{(a\alpha)_i} \frac{\partial(a\alpha)_i}{\partial T} + \frac{1}{(a\alpha)_j} \frac{\partial(a\alpha)_j}{\partial T} \right] \quad (33)$$

Taking the derivative with respect to temperature a second times goes as follows

$$\begin{aligned} \frac{\partial^2(a\alpha)_{ij}}{\partial T^2} &= \frac{1}{2} \frac{\partial(a\alpha)_{ij}}{\partial T} \left[\frac{1}{(a\alpha)_i} \frac{\partial(a\alpha)_i}{\partial T} + \frac{1}{(a\alpha)_j} \frac{\partial(a\alpha)_j}{\partial T} \right] \\ &+ \frac{(a\alpha)_{ij}}{2} \left[\frac{1}{(a\alpha)_i} \frac{\partial^2(a\alpha)_i}{\partial T^2} - \frac{1}{(a\alpha)_i^2} \frac{\partial(a\alpha)_i^2}{\partial T} + \right. \\ &\quad \left. \frac{1}{(a\alpha)_j} \frac{\partial^2(a\alpha)_j}{\partial T^2} - \frac{1}{(a\alpha)_j^2} \frac{\partial(a\alpha)_j^2}{\partial T} \right] \end{aligned}$$

The first term can be simplified using (33) giving

$$\begin{aligned} \frac{\partial^2(a\alpha)_{ij}}{\partial T^2} &= \frac{1}{(a\alpha)_{ij}} \frac{\partial(a\alpha)_{ij}^2}{\partial T} + \frac{(a\alpha)_{ij}}{2} \left[\frac{1}{(a\alpha)_i} \frac{\partial^2(a\alpha)_i}{\partial T^2} - \frac{1}{(a\alpha)_i^2} \frac{\partial(a\alpha)_i^2}{\partial T} + \right. \\ &\quad \left. \frac{1}{(a\alpha)_j} \frac{\partial^2(a\alpha)_j}{\partial T^2} - \frac{1}{(a\alpha)_j^2} \frac{\partial(a\alpha)_j^2}{\partial T} \right] \end{aligned} \quad (34)$$

3.3.1 Species Parameters

The first and second derivatives of the species parameters are needed for the mixture derivatives. Since a is not temperature-dependent

$$\frac{\partial(a\alpha)_i}{\partial T} = a_i \frac{\partial\alpha_i}{\partial T} \quad (35)$$

and

$$\frac{\partial^2(a\alpha)_i}{\partial T^2} = a_i \frac{\partial^2\alpha_i}{\partial T^2} \quad (36)$$

Taking the derivative of (6) with respect to temperature

$$\begin{aligned} \frac{\partial\alpha_i}{\partial T} &= \frac{\partial}{\partial T} \left(\left[1 + \kappa_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \right) \\ &= 2 \left[1 + \kappa_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right] \cdot \left(-\frac{\kappa_i}{\sqrt{TT_{c,i}}} \right) \end{aligned}$$

and substituting the first term for the square root of (6) gives

$$\frac{\partial\alpha_i}{\partial T} = -2\kappa_i \sqrt{\frac{\alpha_i}{TT_{c,i}}} \quad (37)$$

Taking the derivative with respect to temperature a second time

$$\begin{aligned} \frac{\partial^2\alpha_i}{\partial T^2} &= \frac{-2\kappa_i}{\sqrt{T_{c,i}}} \frac{\partial}{\partial T} \left(\sqrt{\frac{\alpha_i}{T}} \right) \\ &= \frac{-2\kappa_i}{\sqrt{T_{c,i}}} \left[\frac{1}{2} \sqrt{\frac{T}{\alpha_i}} \left(\frac{1}{T} \frac{\partial\alpha_i}{\partial T} - \frac{\alpha_i}{T^2} \right) \right] \end{aligned}$$

which can be simplified to

$$\frac{\partial^2 \alpha_i}{\partial T^2} = -\kappa_i \sqrt{\frac{\alpha_i}{TT_{c,i}}} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} - \frac{1}{T} \right)$$

the first term can be substituted using (37) to give the final formula

$$\frac{\partial^2 \alpha_i}{\partial T^2} = \frac{1}{2} \frac{\partial \alpha_i}{\partial T} \left(\frac{1}{\alpha_i} \frac{\partial \alpha_i}{\partial T} - \frac{1}{T} \right) \quad (38)$$

References

- [1] David G. Goodwin et al. *Cantera: An Object-oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes*. <https://www.cantera.org>. Version 2.6.0. 2022. DOI: 10.5281/zenodo.6387882.
- [2] Ding-Yu Peng and Donald B Robinson. “A new two-constant equation of state”. In: *Industrial & Engineering Chemistry Fundamentals* 15.1 (1976), pp. 59–64.
- [3] Otto. Redlich and J. N. S. Kwong. “On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions.” In: *Chemical Reviews* 44.1 (1949), pp. 233–244. DOI: 10.1021/cr60137a013.
- [4] Giorgio Soave. “Equilibrium constants from a modified Redlich-Kwong equation of state”. In: *Chemical engineering science* 27.6 (1972), pp. 1197–1203.