

# 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 [4] and Peng-Robinson [3] real gas equations of state. This paper outlines the approach taken to implement the Soave modification of the Redlich-Kwong EoS [5] by building upon the work of Kogekar in implementing the Peng-Robinson EoS [2].

## 2 Equation of State Comparison

Due to the extensive similarities between the Soave-Redlich-Kwong EoS and the Peng-Robinson EoS, many of the necessary derivations require only small modifications, if any. Therefore, a comparison of each EoS is presented in this section as a starting point for the implementation.

### 2.1 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  $\nu$  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  $\Omega_a$  and  $\Omega_b$  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  $\alpha$  is given as

$$\alpha(T) = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2) \left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \quad (6)$$

where  $\omega$  is the acentric factor of the species.

### 2.1.1 Multi-component Soave-Redlich-Kwong EoS

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

$$p = \frac{RT}{\nu - b_{mix}} - \frac{(a\alpha)_{mix}}{\nu(\nu + b_{mix})} \quad (7)$$

The mixture averaged properties are defined as

$$a_{mix} = \sum_i \sum_j X_i X_j a_{ij} \quad (8)$$

$$b_{mix} = \sum_i X_i b_i \quad (9)$$

$$(a\alpha)_{mix} = \sum_i \sum_j X_i X_j (a\alpha)_{ij} \quad (10)$$

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

$$a_{ij} = \sqrt{a_i a_j} \quad (11)$$

$$(a\alpha)_{ij} = \sqrt{(a\alpha)_i (a\alpha)_j} \quad (12)$$

## 2.2 Peng-Robinson EoS

The Peng-Robinson (PR) EoS is given by

$$p = \frac{RT}{\nu - b} - \frac{a\alpha}{\nu^2 + 2b\nu - b^2} \quad (13)$$

where the parameters  $a$  and  $b$  are defined as

$$a = \frac{a_0 R^2 T_c^2}{p_c} \quad (14)$$

$$b = \frac{b_0 RT_c}{p_c} \quad (15)$$

where the constants  $a_0$  and  $b_0$  are calculated from the cubic solution as

$$a_0 = 0.45723552888 \quad (16)$$

$$b_0 = 0.0777960738922 \quad (17)$$

The temperature dependent interaction term  $\alpha$  is defined as

$$\alpha(T) = \left[ 1 + \kappa \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (18)$$

where  $\kappa$  is a piecewise function of the acentric factor  $\omega$

$$\kappa = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2, & \text{if } \omega \leq 0.491 \\ 0.379642 + 1.487503\omega - 0.164423\omega^2 + 0.016666\omega^3, & \text{if } \omega > 0.491 \end{cases} \quad (19)$$

## 2.3 Comparison

Summarized below are the main observations:

- The primary difference between the SRK and PR equations of state is the denominator of the second term in the EoS, given in (1) and (13), respectively. The equations of state will thus have slightly different cubic forms and derivatives of pressure with respect to molar volume and temperature.
- The definitions of the  $a$  and  $b$  terms are identical, with the exception of different values for the constants  $\Omega_a$  and  $\Omega_b$ . Therefore, calculation of the critical properties from these parameters will utilize the same equations.
- Similarly, the temperature dependent interaction terms  $\alpha$  only differ by the definition of  $\kappa$ , which is a function of only the acentric factor. Thus, derivatives of  $\alpha$  with respect to temperature will be of the same form, albeit with different values of  $\kappa$ .

The required derivations for those equations that will take a different form than the current implementation of the PR EoS are performed below.

## 3 Derivations

### 3.1 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

$$\nu^3 - \frac{RT}{p}\nu^2 + \left(\frac{a\alpha - bRT}{p} - b^2\right)\nu - \frac{a\alpha b}{p} = 0 \quad (20)$$

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

$$Z = \frac{P\nu}{RT} \quad (21)$$

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

$$\nu = \frac{ZRT}{P} \quad (22)$$

into (20) 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

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (23)$$

where the terms  $A$  and  $B$  are given by

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

$$B = \frac{bp}{RT} \quad (25)$$

### 3.2 Derivatives of $p$

The pressure derivatives of the multi-component SRK equation of state (7) with respect to  $\nu$  and  $T$  are given by

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

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

### 3.3 Derivatives of $\nu$

The required derivatives of  $\nu$  can be obtained from the cubic equation in terms of molar volume (20), or alternatively by taking the derivatives of the cubic equation as a function of compressibility factor (23) and using the relationship (22).

#### 3.3.1 Isothermal Compressibility

Isothermal compressibility is defined as

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

The derivative of molar volume from (22) with respect to pressure is

$$\begin{aligned} \left( \frac{\partial \nu}{\partial p} \right)_T &= \frac{pRT \left( \frac{\partial Z}{\partial p} \right)_T - ZRT}{p^2} \\ \left( \frac{\partial \nu}{\partial p} \right)_T &= \frac{RT}{p} \left( \frac{\partial Z}{\partial p} \right)_T - \frac{\nu}{p} \end{aligned} \quad (29)$$

Substituting into (28) yields isothermal compressibility as a function of compressibility factor

$$\begin{aligned} \beta_T &= -\frac{1}{\nu} \left[ \frac{RT}{p} \left( \frac{\partial Z}{\partial p} \right)_T - \frac{\nu}{p} \right] \\ \beta_T &= \frac{1}{p} - \frac{1}{Z} \left( \frac{\partial Z}{\partial p} \right)_T \end{aligned} \quad (30)$$

Then, taking the derivative of (23) with respect to pressure gives

$$\begin{aligned} 3Z^2 \left( \frac{\partial Z}{\partial P} \right)_T - 2Z \left( \frac{\partial Z}{\partial P} \right)_T + (A - B - B^2) \left( \frac{\partial Z}{\partial P} \right)_T \\ + \left[ \left( \frac{\partial A}{\partial P} \right)_T - \left( \frac{\partial B}{\partial P} \right)_T - 2B \left( \frac{\partial B}{\partial P} \right)_T \right] Z \\ - A \left( \frac{\partial B}{\partial P} \right)_T - B \left( \frac{\partial A}{\partial P} \right)_T = 0 \end{aligned}$$

rearranging gives

$$\left( \frac{\partial Z}{\partial P} \right)_T = \frac{(B - Z) \left( \frac{\partial A}{\partial P} \right)_T + (A + B + 2BZ) \left( \frac{\partial B}{\partial P} \right)_T}{3Z^2 - 2Z + A - B - B^2} \quad (31)$$

where the derivatives of (24) and (25) are straightforward to calculate

$$\left( \frac{\partial A}{\partial P} \right)_T = \frac{a\alpha}{R^2 T^2} = \frac{A}{p} \quad (32)$$

$$\left( \frac{\partial B}{\partial P} \right)_T = \frac{b}{RT} = \frac{B}{p} \quad (33)$$

### 3.3.2 Thermal Expansion Coefficient

The volumetric thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{\nu} \left( \frac{\partial \nu}{\partial T} \right)_p \quad (34)$$

Taking a similar approach as for the isothermal compressibility, the derivative of molar volume with respect to temperature is

$$\left( \frac{\partial \nu}{\partial T} \right)_p = \frac{ZR}{P} + \frac{RT}{p} \left( \frac{\partial Z}{\partial T} \right)_p \quad (35)$$

substituting into (34) yields thermal expansion coefficient in terms of compressibility factor

$$\begin{aligned} \alpha_V &= \frac{1}{\nu} \left[ \frac{ZR}{P} + \frac{RT}{p} \left( \frac{\partial Z}{\partial T} \right)_p \right] \\ \alpha_V &= \frac{1}{T} + \frac{1}{Z} \left( \frac{\partial Z}{\partial T} \right)_p \end{aligned} \quad (36)$$

Then, taking the derivative of (23) with respect to temperature will yield an identical equation to (31) with the appropriate derivatives

$$\left( \frac{\partial Z}{\partial T} \right)_p = \frac{(B - Z) \left( \frac{\partial A}{\partial T} \right)_P + (A + B + 2BZ) \left( \frac{\partial B}{\partial T} \right)_P}{3Z^2 - 2Z + A - B - B^2} \quad (37)$$

The derivatives of  $A$  and  $B$  are likewise straightforward, but it must be noted that  $a\alpha$  is a function of temperature when taking the derivative of  $A$

$$\left( \frac{\partial A}{\partial P} \right)_T = \frac{p}{R^2 T^2} \left[ \left( \frac{\partial(a\alpha)}{\partial T} \right)_P - \frac{2a\alpha}{T} \right] \quad (38)$$

$$\left( \frac{\partial B}{\partial P} \right)_T = -\frac{bp}{RT^2} = -\frac{B}{T} \quad (39)$$

## 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.
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