Compressibility Derivatives
Peng-Robinson and Redlich-Kwong

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1 Definitions

The compressibility factor is given by

$$Z = \frac{\nu p}{RT} \tag{1}$$

where ν is molar volume, p is pressure, R is the gas constant, and T is temperature. This can also be written in terms of the molar volume

$$\nu = \frac{ZRT}{p} \tag{2}$$

1.1 Isothermal Compressibility

Isothermal compressibility is defined as

$$\beta_T = -\frac{1}{\nu}\left(\frac{\partial \nu}{\partial p}\right)_T \tag{3}$$

This can alternatively be expressed in terms of the compressibility factor, which requires the derivative of (2) with respect to pressure at constant temperature

$$\left(\frac{\partial \nu}{\partial p}\right)_T = \frac{pRT\left(\frac{\partial Z}{\partial p}\right)_T - ZRT}{p^2}$$

$$\left(\frac{\partial \nu}{\partial p}\right)_T = \frac{RT}{p}\left(\frac{\partial Z}{\partial p}\right)_T - \frac{\nu}{p} \tag{4}$$

Substituting into (3) yields isothermal compressibility as a function of compressibility factor

$$\beta_T = -\frac{1}{\nu}\left[\frac{RT}{p}\left(\frac{\partial Z}{\partial p}\right)_T - \frac{\nu}{p}\right]$$

$$\beta_T = \frac{1}{p} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_T \tag{5}$$

where the first term is the ideal component and the second term is the real gas deviation.

1.2 Thermal Expansion Coefficient

The volumetric thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{\nu}\left(\frac{\partial \nu}{\partial T}\right)_p \tag{6}$$

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

$$\left(\frac{\partial \nu}{\partial T}\right)_p = \frac{ZR}{P} + \frac{RT}{p}\left(\frac{\partial Z}{\partial T}\right)_p \tag{7}$$

substituting into (6) yields thermal expansion coefficient in terms of compressibility factor

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

$$\alpha_V = \frac{1}{T} + \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_p \tag{8}$$

where the first term is the ideal component and the second term is the real gas deviation.

2 Peng-Robinson

The cubic form of the Peng-Robinson equation of state is given by

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \tag{9}$$

where

$$A = \frac{a\alpha p}{R^2T^2} \tag{10}$$

and

$$B = \frac{bp}{RT} \tag{11}$$

2.1 Isothermal Compressibility

Taking the derivative of (9) with respect to pressure at constant temperature

$$\begin{aligned} 3Z^2\left(\frac{\partial Z}{\partial p}\right)_T - 2Z(1-B)\left(\frac{\partial Z}{\partial p}\right)_T + Z^2\left(\frac{\partial B}{\partial p}\right)_T + (A - 2B - 3B^2)\left(\frac{\partial Z}{\partial p}\right)_T \\ + Z\left[\left(\frac{\partial A}{\partial p}\right)_T - 2\left(\frac{\partial B}{\partial p}\right)_T - 6B\left(\frac{\partial B}{\partial p}\right)_T\right] - A\left(\frac{\partial B}{\partial p}\right)_T - B\left(\frac{\partial A}{\partial p}\right)_T \\ + 2B\left(\frac{\partial B}{\partial p}\right)_T + 3B^2\left(\frac{\partial B}{\partial p}\right)_T = 0 \end{aligned}$$

combining like terms gives

$$\left[3Z^2 - 2Z(1-B) + A - 2B - 3B^2\right]\left(\frac{\partial Z}{\partial p}\right)_T + (Z-B)\left(\frac{\partial A}{\partial p}\right)_T$$
$$+(Z^2 - 2Z - 6BZ - A + 2B + 3B^2)\left(\frac{\partial B}{\partial p}\right)_T = 0$$

then solving for the derivative of the compressibility factor yields

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{(B-Z)\left(\frac{\partial A}{\partial p}\right)_T + (A - 2B - 3B^2 + 2Z + 6BZ - Z^2)\left(\frac{\partial B}{\partial p}\right)_T}{3Z^2 - 2Z(1-B) + A - 2B - 3B^2} \tag{12}$$

where there derivatives of (10) and (11) are given by

$$\left(\frac{\partial A}{\partial p}\right)_T = \frac{a\alpha}{R^2T^2} = \frac{A}{p} \tag{13}$$

and

$$\left(\frac{\partial B}{\partial p}\right)_T = \frac{b}{RT} = \frac{B}{p} \tag{14}$$

2.2 Thermal Expansion Coefficient

The derivative of (9) with respect to temperature at constant pressure will take the same form as (12)

$$\left(\frac{\partial Z}{\partial T}\right)_p = \frac{(B-Z)\left(\frac{\partial A}{\partial T}\right)_p + (A - 2B - 3B^2 + 2Z + 6BZ - Z^2)\left(\frac{\partial B}{\partial T}\right)_p}{3Z^2 - 2Z(1-B) + A - 2B - 3B^2} \tag{15}$$

where the derivative of (10) using the quotient rule is given by

$$\left(\frac{\partial A}{\partial T}\right)_p = \frac{p}{R^2}\left[\frac{T^2\left(\frac{\partial a\alpha}{\partial T}\right)_p - 2a\alpha T}{T^4}\right]$$
$$\left(\frac{\partial A}{\partial T}\right)_p = \frac{p}{R^2T^2}\left[\left(\frac{\partial a\alpha}{\partial T}\right)_p - \frac{2a\alpha}{T}\right] \tag{16}$$

and the derivative of (11) is given by

$$\left(\frac{\partial B}{\partial T}\right)_p = -\frac{bP}{RT^2} = -\frac{B}{T} \tag{17}$$

3 Redlich-Kwong

The cubic form is given by

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \tag{18}$$

where

$$A = \frac{ap}{R^2 T^{2.5}} \tag{19}$$

and

$$B = \frac{bp}{RT} \tag{20}$$

3.1 Isothermal Compressibility

Taking the derivative of (18) with respect to pressure at constant temperature

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

combining like terms gives

$$\left[3Z^2 - 2Z + A - B - B^2\right]\left(\frac{\partial Z}{\partial p}\right)_T + (Z - B)\left(\frac{\partial A}{\partial p}\right)_T - (A + Z + 2BZ)\left(\frac{\partial B}{\partial p}\right)_T = 0$$

then rearranging to solve for the derivative of the compressibility factor yields

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{(B - Z)\left(\frac{\partial A}{\partial p}\right)_T + (A + Z + 2BZ)\left(\frac{\partial B}{\partial p}\right)_T}{3Z^2 - 2Z + A - B - B^2} \tag{21}$$

where the derivatives of (19) and (20) are given by

$$\left(\frac{\partial A}{\partial p}\right)_T = \frac{a}{R^2 T^{2.5}} = \frac{A}{p} \tag{22}$$

and

$$\left(\frac{\partial B}{\partial p}\right)_T = \frac{b}{RT} = \frac{B}{p} \tag{23}$$

3.2 Thermal Expansion Coefficient

The derivative of (18) with respect to temperature at constant pressure will take the same form as (21)

$$\left(\frac{\partial Z}{\partial T}\right)_p = \frac{(B - Z)\left(\frac{\partial A}{\partial T}\right)_p + (A + Z + 2BZ)\left(\frac{\partial B}{\partial T}\right)_p}{3Z^2 - 2Z + A - B - B^2} \tag{24}$$

where the derivative of (19) using the quotient rule is given by

$$\left(\frac{\partial A}{\partial T}\right)_p = \frac{p}{R^2}\left[\frac{T^{2.5}\left(\frac{\partial a}{\partial T}\right)_p - 2.5aT^{1.5}}{T^5}\right]$$

$$\left(\frac{\partial A}{\partial T}\right)_p = \frac{p}{R^2T^{2.5}}\left[\left(\frac{\partial a}{\partial T}\right)_p - \frac{2.5a}{T}\right]$$

$$\left(\frac{\partial A}{\partial T}\right)_p = A\left[\frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_p - \frac{2.5}{T}\right] \tag{25}$$

and the derivative of (20) is given by

$$\left(\frac{\partial B}{\partial T}\right)_p = -\frac{bp}{RT^2} = -\frac{B}{T} \tag{26}$$