1 Peng-Robinson

The Peng-Robinson equation of state is

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

where ν is the molar volume, T_c is the critical temperature, P_c is the critical pressure, ω is the acentric factor, and where

$$a = a_c \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right] \tag{2}$$

$$a_c = 0.45723553\frac{R^2{T_c}^2}{P_c} \tag{3}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

$$b = 0.077796074\frac{RT_c}{P_c} \tag{5}$$

The cubic polynomial form of the compressibility factor is

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \tag{6}$$

where

$$\alpha = B - 1 \tag{7}$$

$$\beta = A - 2B - 3B^2 \tag{8}$$

$$\gamma = B^3 + B^2 - AB \tag{9}$$

and

$$A = \frac{aP}{(RT)^2} \tag{10}$$

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

1.1 Isothermal Compressibility

Isothermal compressibility is defined as

$$\kappa = -\frac{1}{\nu}\left(\frac{\partial \nu}{\partial P}\right)_T \tag{12}$$

Taking the derivative of (6) with respect to pressure at constant temperature yields

$$3Z^2\left(\frac{\partial Z}{\partial P}\right)_T + 2\alpha Z\left(\frac{\partial Z}{\partial P}\right)_T + Z^2\left(\frac{\partial \alpha}{\partial P}\right)_T + \beta\left(\frac{\partial Z}{\partial P}\right)_T + Z\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \gamma}{\partial P}\right)_T = 0$$

which simplifies to

$$\left(\frac{\partial Z}{\partial P}\right)_T = -\frac{Z^2\left(\frac{\partial \alpha}{\partial P}\right)_T + Z\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \gamma}{\partial P}\right)_T}{3Z^2 + 2\alpha Z + \beta} \tag{13}$$

the compressibility factor and molar volume are related by

$$Z = \frac{P\nu}{RT} \tag{14}$$

Therefore, molar volume can be expressed as

$$\nu = \frac{ZRT}{P} \tag{15}$$

The derivative of molar volume with respect to pressure at constant temperature is then

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

which simplifies to

$$\left(\frac{\partial \nu}{\partial P}\right)_T = \nu\left[\frac{1}{Z}\left(\frac{\partial Z}{\partial P}\right)_T - \frac{1}{P}\right] \tag{16}$$

Therefore, equations (13) and (16) can be used to calculate isothermal compressibility given the corresponding derivatives of α, β, and γ. From equations (7-9) the following derivatives are readily available

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \left(\frac{\partial B}{\partial P}\right)_T \tag{17}$$

$$\left(\frac{\partial \beta}{\partial P}\right)_T = \left(\frac{\partial A}{\partial P}\right)_T - 2(1+3B)\left(\frac{\partial B}{\partial P}\right)_T \tag{18}$$

$$\left(\frac{\partial \gamma}{\partial P}\right)_T = (3B^2 + 2B - A)\left(\frac{\partial B}{\partial P}\right)_T - B\left(\frac{\partial A}{\partial P}\right)_T \tag{19}$$

Finally, from equations (10) and (11) the last two required derivatives are defined as

$$\left(\frac{\partial A}{\partial P}\right)_T = \frac{a}{(RT)^2} \tag{20}$$

$$\left(\frac{\partial B}{\partial P}\right)_T = \frac{b}{RT} \tag{21}$$