Example 02.09 Density of Propylene from the Peng-Robinson Equation of State

problem:

Calculate the density of propylene at $T = 300\,\mathrm{K}$ and $P = 10$ bar using the Peng–Robinson equation of state. The vapor pressure of propylene is $P^s(300\,\mathrm{K}) = 12.1$ bar.

general constants and definitions:

$kPa := 1000Pa \qquad R_{gas} := 8.31433 \frac{J}{K \cdot mol} \qquad bar := 100kPa \qquad dm := 0.1m$

$grm := 0.001kg$

input data

$T := 300K \qquad P := 10bar$

From Appendix A: $T_c := 365.570K \qquad P_c := 46.646bar \qquad \omega := 0.1408$

$mw := 42.081 \frac{grm}{mol}$

Solution

The Peng-Robinson EOS can be written as:

$$P_{PR} = \frac{R_{gas} \cdot T}{v - b} - \frac{a \cdot \alpha(T)}{v \cdot (v + b) + b \cdot (v - b)}$$

with

$$a := 0.45724 \cdot \frac{R_{gas}^2 \cdot T_c^2}{P_c} \qquad a = 0.906\,m^3\,mol^{-2}\,J$$

$$\alpha(T) := \left[1 + \left(0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2\right) \cdot \left[1 - \left(\frac{T}{T_c}\right)^{0.5}\right]\right]^2$$

$$\alpha(T) = 1.113426 \qquad a \cdot \alpha(T) = 1.008293\,m^3\,mol^{-2}\,J$$

$$b := 0.0778 \cdot \frac{R_{gas} \cdot T_c}{P_c} \qquad b = 5.0695 \times 10^{-5}\,m^3\,mol^{-1}$$

Now all parameters are available and the function can be defined:

$$P_{PR}(v, T) := \left[\frac{R_{gas} \cdot T}{v - b} - \frac{a \cdot \alpha(T)}{v \cdot (v + b) + b \cdot (v - b)}\right]$$

At 300K, the vapor pressure of propylene is higher than the system pressure of 10 bar. The ideal gas volume can be used as starting value for the root function:

$$v := \frac{R_{gas} \cdot T}{P} \qquad v = 2.494 \times 10^{-3}\, m^3\, mol^{-1}$$

The volume at which the Peng-Robinson EOS calculates a pressure of 10 bar can be found via:

$$v := root\left(P_{PR}(v,T) - P, v\right) \qquad v = 2.0972\, mol^{-1}\, dm^3$$

Application of Cardano's Formula

Similar to the Vieta's formula for cubic equations, Cardano'f formula allows to solve cubic equations analytically (see Appendix C, A10).
In the first step the equation should be braucht into the normal form:

$$z^3 + U \cdot z^2 + S \cdot z + T = 0$$

In case of the Peng/Robinson EOS, the coefficients can be calculated as

$$U_{Car} := \frac{b \cdot P}{R_{gas} \cdot T} - 1 \qquad U_{Car} = -0.979676$$

$$S_{Car} := \frac{a \cdot \alpha(T) \cdot P}{R_{gas}^2 \cdot T^2} - 3 \cdot \left(\frac{b \cdot P}{R_{gas} \cdot T}\right)^2 - 2 \cdot \frac{b \cdot P}{R_{gas} \cdot T} \qquad S_{Car} = 0.120177$$

$$T_{Car} := \left(\frac{b \cdot P}{R_{gas} \cdot T}\right)^3 + \left(\frac{b \cdot P}{R_{gas} \cdot T}\right)^2 - \frac{a \cdot \alpha(T) \cdot P}{R_{gas}^2 \cdot T^2} \cdot \frac{b \cdot P}{R_{gas} \cdot T} \qquad T_{Car} = -0.00287238$$

The terms in Cardano's formula can be calculated via:

$$P_{Car} := \frac{3 \cdot S_{Car} - U_{Car}^2}{3} \qquad P_{Car} = -0.199744$$

$$Q_{Car} := \frac{2 \cdot U_{Car}^3}{27} - \frac{U_{Car} \cdot S_{Car}}{3} + T_{Car} \qquad Q_{Car} = -0.033276$$

This yields a negative discriminant D_{Car} (3 real solutions):

$$D_{Car} := \left(\frac{P_{Car}}{3}\right)^3 + \left(\frac{Q_{Car}}{2}\right)^2 \qquad D_{Car} = -1.833474 \times 10^{-5}$$

Solution for the roots yields:

Abbreviations:

$$\Theta := \sqrt{\frac{-P_{Car}^{3}}{27}} \qquad \Theta = 0.017180$$

$$\Phi := \operatorname{acos}\left(\frac{-Q_{Car}}{2 \cdot \Theta}\right) \qquad \Phi = 0.251890$$

$$z := \begin{bmatrix} \left(2 \cdot \Theta^{\frac{1}{3}} \cdot \cos\left(\frac{\Phi}{3} + \frac{2 \cdot \pi}{3}\right)\right) - \frac{U_{Car}}{3} \\ \left(2 \cdot \Theta^{\frac{1}{3}} \cdot \cos\left(\frac{\Phi}{3} + \frac{4 \cdot \pi}{3}\right)\right) - \frac{U_{Car}}{3} \\ \left(2 \cdot \Theta^{\frac{1}{3}} \cdot \cos\left(\frac{\Phi}{3}\right)\right) - \frac{U_{Car}}{3} \end{bmatrix} \qquad z = \begin{pmatrix} 0.032 \\ 0.107 \\ 0.841 \end{pmatrix}$$

$$v := \frac{z \cdot R_{gas} \cdot T}{P} \qquad v = \begin{pmatrix} 7.969917 \times 10^{-5} \\ 2.666789 \times 10^{-4} \\ 2.097226 \times 10^{-3} \end{pmatrix} m^{3}\, mol^{-1}$$

Application of the Polyroots-Function

The polyroots-Function allows to calculate all roots of a polynomial via the LaGuerre or the companion matrix method:

$$z := \operatorname{polyroots}\left(\begin{pmatrix} T_{Car} \\ S_{Car} \\ U_{Car} \\ 1 \end{pmatrix}\right) \qquad z = \begin{pmatrix} 0.03195 \\ 0.10692 \\ 0.84081 \end{pmatrix}$$

$$v := \frac{z \cdot R_{gas} \cdot T}{P} \qquad v = \begin{pmatrix} 7.969917 \times 10^{-5} \\ 2.666789 \times 10^{-4} \\ 2.097226 \times 10^{-3} \end{pmatrix} m^{3}\, mol^{-1}$$

All three methods naturally lead to the same results. The highest calculated volume is the vapor volume. As propylene is below its vapor prealculated asssure, the liquid solution is not stable. The medium value solution is always unstable. The molar density can be calculated as

$$\rho := \frac{1}{v_3} \qquad \rho = 476.820\ \mathrm{mol\,m^{-3}}$$

For the mass density we find:

$$\rho_m := \frac{mw}{v_3} \qquad \rho_m = 20.065\ \mathrm{kg\,m^{-3}}$$

The result from a high precision equation of state is 20.06 kg/m^3. Similarly good results can only be expected for vapor phase densities.