Example 05.11 Liquid Density Using the Peng-Robinson EOS

problem: Calculate the liquid density of cyclohexane at the normal boiling point (T = 353.85K, P = 1 atm) with the help of the Peng-Robinson equation of state.

general constants and definitions:

$R_{gas} := 8.31433 \frac{J}{K \cdot mol}$ $\quad bar := 10^5 Pa$ $\quad dm := 0.1m$ $\quad kmol := 1000mol$

$g := 0.001kg$

input data

Normal boiling temperature of cyclohexane: $T := 353.85K$

Normal atmospheric pressure: $P := 1atm$

Molecular weight: $M_W := 84.16 \frac{kg}{kmol}$

Critical data and acentric factor of cyclohexane:

$T_c := 553.60K$ $\quad P_c := 40.750bar$ $\quad \omega := 0.2092$

Solution

In the first step, the EOS-parameters a and b bave to be calculated from the critical data and the acentric factor:

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

$$a_{PR}(T) := 0.45724 \cdot \frac{R_{gas}^2 \cdot T_c^2}{P_c} \cdot \alpha_{PR}(T)$$

$$b_{PR} := 0.0778 \cdot \frac{R_{gas} \cdot T_c}{P_c}$$

$$\alpha_{PR}(T) = 1.294 \qquad a_{PR}(T) = 30.7556 \frac{\left(dm^3\right)^2 \cdot bar}{mol^2} \qquad b_{PR} = 0.087877 \frac{dm^3}{mol}$$

With all constants available, the Peng-Robinson EOS can now be solved for the liquid volume solution.

$$P_{PR}(T, v) := \frac{R_{gas} \cdot T}{v - b_{PR}} - \frac{a_{PR}(T)}{v \cdot \left(v + b_{PR}\right) + b_{PR} \cdot \left(v - b_{PR}\right)}$$

The equation can conveniently be solved using the root function with a starting value a little above the densest packing volume b_{PR}:

$$v := 1.5 \cdot b_{PR} \qquad v := \mathrm{root}\left(P - P_{PR}(T, v), v\right)$$

$$v = 0.11087 \frac{dm^3}{mol} \qquad P_{PR}(T, v) = 1.013\,bar$$

Dividing the molecular weight by the liquid volume yields the density of liquid cyclohexane at the normal boiling point:

$$\rho := \frac{M_w}{v} \qquad \rho = 759.09 \frac{g}{dm^3}$$

This differs by about 5.6% from the experimental density of 719 g/cm^3 (McCoubrey J.C., McCrea J.N., Ubbelohde A.R., J.Chem.Soc.London, 1961-1971, 1951).

$$\frac{759.09 - 719}{719} \cdot 100 = 5.576$$