Example P02.01 Compressibility Factor and Molar Volume of Methanol Steam

problem:

Calculate the compressibility factor and the molar volume of methanol steam at 200°C and 10 bar

a) using the ideal gas law

b) with the virial equation truncated after the 3rd virial coefficient

general constants and definitions:

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

(using R instead of R_{gas} as the symbol for the ideal gas constant reduces the size and readability of more complex expressions but overwrites the unit definition of R (Rankine))

input data

$T := (273.15 + 200)\mathrm{K} \qquad P := 10\mathrm{bar}$

$B := -219\,\frac{\mathrm{cm}^3}{\mathrm{mol}} \qquad C := -17300\,\frac{\mathrm{cm}^6}{\mathrm{mol}^2}$

Solution

Solution by using the ideal gas law:

$v_m := \frac{R\cdot T}{P} \qquad v_m = 3.934\,\mathrm{mol}^{-1}\,\mathrm{dm}^3$

$z = 1$ by definition

Solution by using the virial equation:

$$\frac{P\cdot v}{R\cdot T} = 1 + B\cdot\frac{1}{v} + C\cdot\left(\frac{1}{v}\right)^2$$

The tolerance has to be decreased for receiving a more precise result.

$TOL := 10^{-18}$

For solving the equation the root-function is used. Finding the root requires a starting value for the volume:.

$v := \frac{R\cdot T}{P} \qquad v = 3.934\,\frac{\mathrm{dm}^3}{\mathrm{mol}}$

$$v_m := \mathrm{root}\left[\frac{P\cdot v}{R\cdot T} - 1 - B\cdot\frac{1}{v} - C\cdot\left(\frac{1}{v}\right)^2, v\right] \qquad v_m = 3.695834\,\frac{\mathrm{dm}^3}{\mathrm{mol}}$$

$$z := \frac{P \cdot v_m}{R \cdot T} \qquad z = 0.93948$$

For not too high pressures where the effect of the 3rd virial coefficient is not predominant, fast convergence can be achived by iterating the value of v_it:

$$v\_it := \frac{R \cdot T}{P} \qquad v\_it = 3.934 \frac{dm^3}{mol}$$

$$\frac{P \cdot v}{R \cdot T} = 1 + B \cdot \frac{1}{v} + C \cdot \frac{1}{v} \cdot \frac{1}{v\_it}$$

The solution of interest for v (and at the same time v_it for the next iteration) of this quadratic equation in v can be found via "Symbolics, Variable, Solve". The cursor has to be on one of the "v" variable symbols in the equation above:

$$v\_it := \frac{1}{2 \cdot P \cdot v\_it} \cdot \left[R \cdot T \cdot v\_it + [R \cdot T \cdot v\_it \cdot (R \cdot T \cdot v\_it + 4 \cdot P \cdot v\_it \cdot B + 4 \cdot P \cdot C)]^{\frac{1}{2}} \right]$$

$$v\_it = 3.696157 \frac{dm^3}{mol} \qquad v\_it - v_m = 3.223 \times 10^{-4} \frac{dm^3}{mol}$$

Solving the equation again with this improved value of v_it leads to nearly the exact result:

$$v\_it := \frac{1}{2 \cdot P \cdot v\_it} \cdot \left[R \cdot T \cdot v\_it + [R \cdot T \cdot v\_it \cdot (R \cdot T \cdot v\_it + 4 \cdot P \cdot v\_it \cdot B + 4 \cdot P \cdot C)]^{\frac{1}{2}} \right]$$

$$v\_it = 3.695835 \frac{dm^3}{mol} \qquad v\_it - v_m = 4.644 \times 10^{-7} \frac{dm^3}{mol}$$

In order to find an analytic solution, first apply the operation "Symbolics - Factor"

$$\frac{P \cdot v}{R \cdot T} - 1 - B \cdot \frac{1}{v} - C \cdot \left(\frac{1}{v}\right)^2 = 0$$

to yield the following expression:

$$\frac{\left(P \cdot v^3 - R \cdot T \cdot v^2 - B \cdot R \cdot T \cdot v - C \cdot R \cdot T\right)}{R \cdot T \cdot v^2} = 0$$