Chemical Thermodynamics for Process Simulation
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Example 02.08_d Pressure of Steam Using a High Precision Equation of State

Problem:

A pressurized vessel (V = 0.5 m^3) contains 5 kg steam (H_2O) at = 220°C. Calculate the pressure in the vessel

a) according to the ideal gas law
b) using the virial equation
c) using the Soave-Redlich-Kwong equation
d) using a high-precision equation of state

$grm := 0.001kg$

molar mass: $mw := 18.015 \frac{grm}{mol}$

2nd virial coefficient: $B := -293 \frac{cm^3}{mol}$

critical temperature: $T_c := 647.096K$

critical pressure: $P_c := 22064105Pa$

acentric factor: $\omega := 0.3443$

Definitions and Constants:

$cm := 0.01m$ $kmol := 1000mol$ $kPa := 1000Pa$ $bar := 10^5 Pa$ $R_{gas} := 8.31433 \frac{J}{mol \cdot K}$

$dm := 0.1m$

Solution:

5 kg of water correspond to a molar quantity of $n := \frac{5kg}{mw}$ $n = 277.54649\,mol$

The volume is $V := 0.5m^3$ and the temperature is $T := (273.15 + 220)K$

This leads to a molar volume of $v := \frac{V}{n}$ $v = 1.80150 \times 10^{-3} m^3 mol^{-1}$

Ideal Gas Law

Using the ideal gas law, the pressure is calculates as:

$P_{IG} := \frac{R_{gas} \cdot T}{v}$ $P_{IG} = 22.75999\,bar$

Virial Equation

As obvious from the unit of the second virial coefficient B, the following form of the equation has to be used (Leiden form):

$$z = 1 + B \cdot \frac{1}{v} \qquad \text{or} \qquad \frac{P \cdot v}{R_{gas} \cdot T} = 1 + B \cdot \frac{1}{v}$$

Solving the right hand side formulation for the pressure P using Symbolics - Variable - Solve leads to:

$$P_{Vir} := \frac{(v + B)}{v^2} \cdot R_{gas} \cdot T \qquad P_{Vir} = 19.05825\,\text{bar}$$

Soave-Redlich-Kwong Equation of State

In case of the Redlich-Kwong-equation the parameters a and b need to be first calculated from the critical temperature and pressure

$$a := 0.42748 \cdot \frac{R_{gas}^{2} \cdot T_c^{2.5}}{P_c} \qquad a = 14.26612\,\text{kg}\,\text{m}^5\,\text{K}^{0.5}\,\text{s}^{-2}\,\text{mol}^{-2}$$

$$b := 0.08664 \frac{R_{gas} \cdot T_c}{P_c} \qquad b = 2.11265 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$$

The pressure can then be calculated directly from the pressure explicit form of the equation:

$$P_{SRK} := \frac{R_{gas} \cdot T}{v - b} - \frac{a}{T^{0.5} v \cdot (v + b)} \qquad P_{SRK} = 21.07355\,\text{bar}$$

The three results are thus:

$$P_{IG} = 22.75999\,\text{bar}$$

$$P_{Vir} = 19.05825\,\text{bar}$$

$$P_{SRK} = 21.07355\,\text{bar}$$

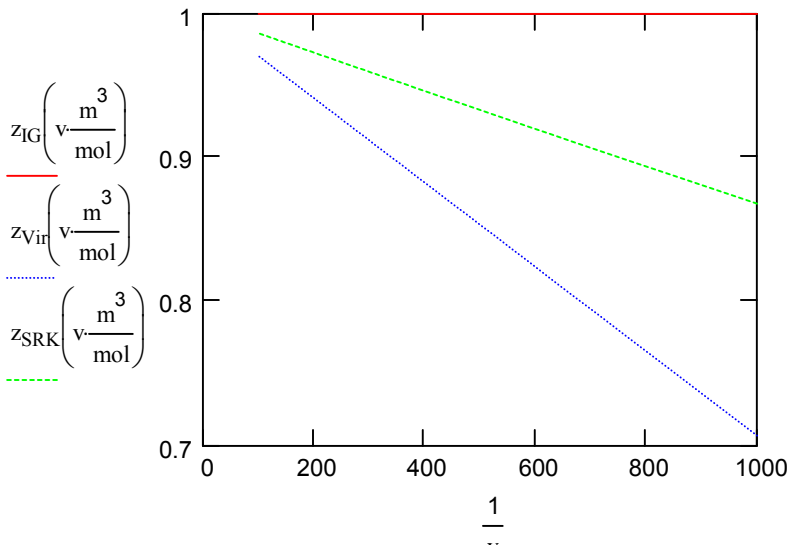
The second virial coefficient is directly fitted to PvT-data and therefor should give reliable results. On the other hand the total pressure is too high for a reliable calculation using only the second virial coefficient. Also in case of the SRK equation, the result might not be reliable at this high pressure.

The correct result calculated via a high precision equation of state is $P_{HiPre} := 20.38170\,\text{bar}$

The vollowing plot shows the compressibility factor as function of reciprocal volume calculated by the three equations above:

$$z_{IG}(v) := 1 \qquad z_{Vir}(v) := \left(1 + B \cdot \frac{1}{v}\right) \qquad z_{SRK}(v) := \frac{v}{v - b} - \frac{a \cdot v}{R_{gas} \cdot T^{1.5} v \cdot (v + b)}$$

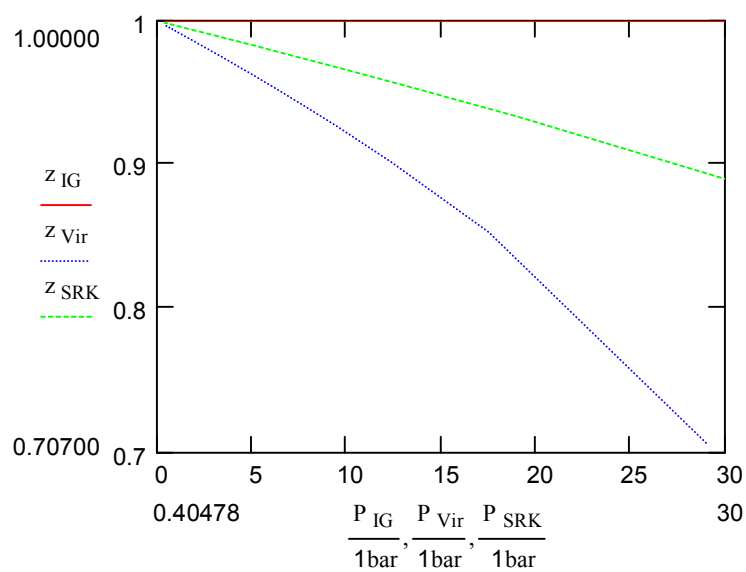
$$v := 10^{-3}, 1.1 \cdot 10^{-3} .. 10^{-2}$$



v

A plot as function of pressure can be generated in the following way:

$$i := 1..101 \quad v_i := i \cdot 10^{-3}\,\frac{m^3}{mol} \quad P_{IG_i} := \frac{R_{gas} \cdot T}{v_i} \qquad z_{IG_i} := \frac{P_{IG_i} \cdot v_i}{R_{gas} \cdot T}$$

$$P_{Vir_i} := \frac{\left(v_i + B\right)}{\left(v_i\right)^2} \cdot R_{gas} \cdot T \qquad z_{Vir_i} := \frac{P_{Vir_i} \cdot v_i}{R_{gas} \cdot T}$$

$$P_{SRK_i} := \frac{R_{gas} \cdot T}{v_i - b} - \frac{a}{T^{0.5}\, v_i \cdot \left(v_i + b\right)} \qquad z_{SRK_i} := \frac{P_{SRK_i} \cdot v_i}{R_{gas} \cdot T}$$