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

molar mass:	M	=	18.015 g/mol
2nd virial coefficient:	B	=	- 293 cm^3/mol
critical temperature:	T_c	=	647.096 K
critical pressure:	P_c	=	220.64 . 105 Pa (220.64 bar)
acentric factor:	ω	=	0.3443

Definitions and Constants:

$cm := 0.01m$ $kmol := 1000mol$ $kPa := 1000Pa$ $bar := 10^5 Pa$

$dm := 0.1m$ $g := 0.001kg$ $kJ := 10^6 Pa$ $h := 3600s$

$MW := 10^6 W$

IAPWS95 Parameters:

IAPWS95 refers to the Revised Release on the "Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (September 2009) as published on the website www.iapws.org of the International Association for the Properties of Water and Steam.
The names of the various constants were transferred to valid MathCad variable names with minor modifications. Details and parameter values can be found in the document:

http://www.iapws.org/relguide/IAPWS95-Rev.pdf (Ref.1)

Critical Data and Gas Constant (Ref.1, page 3):

$T_c := 647.096K$ $\rho_c := 322 \frac{kg}{m^3}$ $R := 461.51805 \frac{J}{kg \cdot K}$

Ideal Gas Parameters (Ref.1, Table 1):

$$n_{id} := \begin{pmatrix} -8.3204464837497 \\ 6.6832105275932 \\ 3.00632 \\ 0.012436 \\ 0.97315 \\ 1.27950 \\ 0.96956 \\ 0.24873 \end{pmatrix} \qquad \gamma A := \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1.28728967 \\ 3.53734222 \\ 7.74073708 \\ 9.24437796 \\ 27.5075105 \end{pmatrix}$$

Dimensionless Helmholtz Free Energy (Ideal Gas) (Ref.1, Equation 5):

$$\alpha_{id}(T,\rho) := \left| \begin{array}{l} \delta \leftarrow \dfrac{\rho}{\rho_c} \\ \tau \leftarrow \dfrac{T_c}{T} \\ A \leftarrow \ln(\delta) + n_{id_1} + n_{id_2} \cdot \tau + n_{id_3} \cdot \ln(\tau) \\ A \leftarrow A + \displaystyle\sum_{i=4}^{8} n_{id_i} \cdot \ln\left(1 - e^{-\gamma A_i \cdot \tau}\right) \end{array} \right.$$

Residual Part Parameters (Ref.1, Table 2):

$$\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \qquad \begin{pmatrix} 1 \\ 1 \\ 1 \\ 2 \\ 2 \\ 3 \\ 4 \\ 1 \\ 1 \\ 1 \\ 2 \end{pmatrix} \qquad \begin{pmatrix} -0.5 \\ 0.875 \\ 1 \\ 0.5 \\ 0.75 \\ 0.375 \\ 1 \\ 4 \\ 6 \\ 12 \\ 1 \end{pmatrix} \qquad \begin{pmatrix} 0.12533547935523 \cdot 10^{-1} \\ 0.78957634722828 \cdot 10 \\ -0.87803203303561 \cdot 10 \\ 0.31802509345418 \\ -0.26145533859358 \\ -0.78199751687981 \cdot 10^{-2} \\ 0.88089493102134 \cdot 10^{-2} \\ -0.66856572307965 \\ 0.20433810950965 \\ -0.66212605039687 \cdot 10^{-4} \\ -0.19232721156002 \\ -0.25709043003438 \\ 0.16074868486251 \\ -0.40092828925807 \cdot 10^{-1} \\ 0.39343422603254 \cdot 10^{-6} \\ -0.75941377088144 \cdot 10^{-5} \\ 0.56250979351888 \cdot 10^{-3} \\ -0.15608652257135 \cdot 10^{-4} \\ 0.11537996422951 \cdot 10^{-8} \end{pmatrix}$$

$$cA := \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 3 \\ 3 \\ 3 \\ 3 \\ 4 \\ 6 \end{vmatrix} \quad dA := \begin{vmatrix} 2 \\ 3 \\ 4 \\ 4 \\ 5 \\ 7 \\ 9 \\ 10 \\ 11 \\ 13 \\ 15 \\ 1 \\ 2 \\ 2 \\ 2 \\ 3 \\ 4 \\ 4 \\ 4 \\ 5 \\ 6 \\ 6 \\ 7 \\ 9 \\ 9 \\ 9 \\ 9 \\ 10 \\ 10 \\ 12 \\ 3 \\ 4 \\ 4 \\ 5 \\ 14 \\ 3 \end{vmatrix} \quad tA := \begin{vmatrix} 5 \\ 4 \\ 2 \\ 13 \\ 9 \\ 3 \\ 4 \\ 11 \\ 4 \\ 13 \\ 1 \\ 7 \\ 1 \\ 9 \\ 10 \\ 3 \\ 7 \\ 10 \\ 10 \\ 6 \\ 10 \\ 10 \\ 1 \\ 2 \\ 3 \\ 4 \\ 8 \\ 6 \\ 9 \\ 8 \\ 16 \\ 22 \\ 23 \\ 23 \\ 10 \\ 50 \end{vmatrix}$$

$$nA := \begin{vmatrix} 0.36582165144204 \cdot 10^{-6} \\ -0.13251180074668 \cdot 10^{-11} \\ -0.62639586912454 \cdot 10^{-9} \\ -0.10793600908932 \\ 0.17611491008752 \cdot 10^{-1} \\ 0.22132295167546 \\ -0.40247669763528 \\ 0.58083399985759 \\ 0.49969146990806 \cdot 10^{-2} \\ -0.31358700712549 \cdot 10^{-1} \\ -0.74315929710341 \\ 0.47807329915480 \\ 0.20527940895948 \cdot 10^{-1} \\ -0.13636435110343 \\ 0.14180634400617 \cdot 10^{-1} \\ 0.83326504880713 \cdot 10^{-2} \\ -0.29052336009585 \cdot 10^{-1} \\ 0.38615085574206 \cdot 10^{-1} \\ -0.20393486513704 \cdot 10^{-1} \\ -0.16554050063734 \cdot 10^{-2} \\ 0.19955571979541 \cdot 10^{-2} \\ 0.15870308324157 \cdot 10^{-3} \\ -0.16388568342530 \cdot 10^{-4} \\ 0.43613615723811 \cdot 10^{-1} \\ 0.34994005463765 \cdot 10^{-1} \\ -0.76788197844621 \cdot 10^{-1} \\ 0.22446277332006 \cdot 10^{-1} \\ -0.62689710414685 \cdot 10^{-4} \\ -0.55714118565645 \cdot 10^{-9} \end{vmatrix}$$

$$\begin{pmatrix} 0 \\ 6 \\ 6 \\ 6 \\ 0 \\ 0 \\ 0 \\ 3.5 \\ 3.5 \end{pmatrix} \quad \begin{pmatrix} 0 \\ 6 \\ 6 \\ 6 \\ 3 \\ 3 \\ 3 \\ 0.85 \\ 0.95 \end{pmatrix} \quad \begin{pmatrix} 36 \\ 44 \\ 46 \\ 50 \\ 0 \\ 1 \\ 4 \\ 0.2 \\ 0.2 \end{pmatrix} \quad \begin{pmatrix} -0.55711118565645 \cdot 10 \\ -0.19905718354408 \\ 0.31777497330738 \\ -0.11841182425981 \\ -0.31306260323435 \cdot 10^{2} \\ 0.31546140237781 \cdot 10^{2} \\ -0.25213154341695 \cdot 10^{4} \\ -0.14874640856724 \\ 0.31806110878444 \end{pmatrix}$$

Residual Part of the Dimensionless Helmholtz Free Energy (Ref.1, Equation 6):

$$\alpha_R(T,\rho) := \left| \begin{array}{l} \delta \leftarrow \dfrac{\rho}{\rho_c} \\ \tau \leftarrow \dfrac{T_c}{T} \\ A \leftarrow \displaystyle\sum_{i=1}^{7} nA_i \cdot \delta^{dA_i} \cdot \tau^{tA_i} \\ A \leftarrow A + \displaystyle\sum_{i=8}^{51} nA_i \cdot \delta^{dA_i} \cdot \tau^{tA_i} \cdot e^{-\delta^{cA_i}} \end{array} \right.$$

Total Dimensionless Helmholtz Free Energy (Ref.1, Equation 4):

$$\alpha(T,\rho) := \alpha_{id}(T,\rho) + \alpha_R(T,\rho)$$

Solution:

The pressure can easily be calculated using the following function (Ref.1, Table 3) :

$$P_{eos}(T,v) := -R \cdot T \cdot \left(\frac{d}{dv}\alpha\left(T, \frac{1}{v}\right)\right)$$

$$P_{eos}\left(493.15K, \frac{1}{10\,\frac{kg}{m^3}}\right) = 20.38170\,bar$$

Expressions for further properties are given in Ref.1, Table 3. Analytical derivatives are reported in Ref.1, Tables 4 and 5.