Problem 1: Calculate V and Z for sulphur hexafluoride at 75°C and 15 bar by the following equations of state:

(a) truncated virial equation,

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

with B = -194 $cm^3.gmol^{-1}$ and C = 15300 $cm^6.gmol^{-2}$;

(b) Redlich-Kwong;

(c) Soave-Redlich-Kwong;

(d) Peng-Robinson.

Sulfur hexafluoride: P_c = 37.6 bar, T_c = 318.7 K, V_c = 198 $cm^3.gmol^{-1}$, ω = 0.286.

Problem 2: Predict the pressure of N_2 gas at 175 K and V = 3.75×10^{-3} $m^3.kg^{-1}$ through the following equations of state:

(a) Ideal gas equation;

(b) van der Waals;

(c) Benedict-Webb-Rubin,

$$P = \frac{RT}{V} + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)V^{-2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right)e^{-\gamma/V^2}$$

with [P] = kPa, [V] = $m^3.kgmol^{-1}$, [T] = K and $R = 8.314\ \frac{\text{kPa.m}^3}{kgmol.K}$

a = 2.54	b = 2.328×10^{-3}	c = 7.379×10^4	α = 1.272×10^{-4}
A_0 = 106.73	B_0 = 0.04074	C_0 = 8.164×10^5	γ = 0.0053

Problem 01:

$$F_6S \begin{cases} \begin{cases} T = 75°C = 348.15\,K \\ P = 15 \text{ bar} \end{cases} \\ \begin{cases} T_c = 318.7\,K \\ P_c = 37.6 \text{ bar} \end{cases} \quad \omega = 0286 \end{cases}$$

(a) Virial EOS:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

$B = -194\ cm^3/gmol$

$C = 15300\ cm^6/gmol^2$

↳ non-linear equation → we need an iterative method to solve this equation for $\underline{V}$ & $\underline{Z}$. As an initial guess, we can assume $V_0 = V^{\text{(ideal gas)}}$

$$V_0 = \frac{RT}{P} = 8.314 \frac{J}{gmol.K} \times \frac{348.15\,K}{15\,bar} \times \frac{1\,bar}{10^5\,N/m^2} \times \frac{1\,Nm}{1\,J} \times \frac{100^3\,cm^3}{1\,m^3}$$

[cm³/gmol]

$$V_0 = 1929.68\ cm^3/gmol$$

Using any root-finding method, e.g., Newton-Raphson:

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)} \qquad (1)$$

until convergence. Thus we can define the function $f(V)$ as

$$f(V) = \frac{PV}{RT} - 1 - \frac{B}{V} - \frac{C}{V^2}$$

the derivative of $f(v)$ with respect of V is.

$$f'(V) = \frac{P}{RT} + \frac{B}{V^2} + \frac{2VC}{V^4}$$

Therefore we need to solve (1) as

$$V_1 = V_0 - \frac{f(V_0)}{f'(V_0)} \qquad (2)$$

Thus $V_1 = 1724.68$ cm³/gmol

$V_2 = 1722.27$ cm³/gmol

$V_3 = 1722.27$ cm³/gmol

converged!!

Now calculating Z,

$$Z = \frac{PV}{RT} = 0.8925$$

(b) Redlich-Kwong EOS:

$$P = \frac{RT}{V-b} - \frac{a}{T_r^{1/2}(V+b)V} \qquad (3)$$

$$a = 0.42748\,\frac{R^2 T_c^2}{P_c} \qquad b = 0.08664\,\frac{R T_c}{P_c}$$

Different from the Virial EOS, writing Eqn (3) to obtain a derivative we could use in Eqn. (1) is not straightforward, thus we can use the general form of the cubic EOS,

$$Z = 1 + \beta - q\beta\,\frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)} \qquad (4)$$

$$P_r = \frac{P}{P_c} = 0.399$$

$$T_r = \frac{T}{T_c} = 1.092$$

$$\beta = \Omega\,\frac{P_r}{T_r} = 0.08664 \times \frac{0.399}{1.092} = 0.0317$$

$$q = \frac{\Psi\,\alpha(T_r)}{\Omega\,T_r} = \frac{0.42748 \times T_r^{-1/2}}{0.08664 \times T_r} = 4.3238$$

$$\varepsilon = 0\ ;\ \sigma = 1$$

We can rewrite Eqn. (4) as

$$F(Z) = Z - 1 - \beta + q\beta\,\frac{Z-\beta}{Z(Z+\beta)} \qquad (5)$$

and

$$\frac{dF}{dZ}(Z) = 1 + \frac{q\beta(Z^2+\beta Z) - Zq\beta(2Z+\beta)}{(Z^2+\beta Z)^2} + \frac{q\beta^2(2Z+\beta)}{(Z^2+\beta Z)^2} \quad (6)$$

Now using Newton-Raphson method:

$$Z_1 = Z_0 - \frac{F(Z_0)}{F'(Z_0)}$$

with $Z_0 = 0.90$ as initial estimative

$Z_1 = 0.888$

$Z_2 = 0.888$

converged!

$Z = 0.888$

Using $Z = PV/RT$ ∴ $V = 1713.56 \; cm^3/gmol$

(c) Soave R-K EOS:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$$

$\alpha = [1 + \gamma(1-\sqrt{T_r})]^2$; $\gamma = 0.48 + 1.574\,\omega - 0.176\,\omega^2$

Now, with similar procedure to (b) – Eqn. (4), but with

$\Omega = 0.08664$ $\qquad \varepsilon = 0$

$\Psi = 0.42748$ $\qquad \sigma = 1$

Thus,

$\beta = 0.0317$; $q = 3.7852$

The expressions for F(z) and dF/dz (z) will be the same as in (b) – Eqns. (6) and (7). With $z_0 = 0.90$

$\boxed{z_1 = 0.8948}$ } converged!

$z_2 = 0.8948$

$V = 1726.68 \ cm^3/gmol$

(d) Peng-Robinson EOS:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}$$

$\gamma = 0.37464 + 1.54226\omega - 0.26992\omega^2$

with

$\Omega = 0.07780$ $\qquad \varepsilon = 1-\sqrt{2}$

$\Psi = 0.45724$ $\qquad \sigma = 1+\sqrt{2}$

Thus,

$\beta = 0.0284$; $q = 5.0045$

Because $\varepsilon \neq 0$ and $\sigma \neq 1$ (in Eq. 4), then Eqn. (5) becomes

$$F(z) = Z - 1 - \beta + q\beta \frac{Z-\beta}{\underbrace{(Z+\varepsilon\beta)(Z+\sigma\beta)}_{K}}$$

$$dF/dz\,(z) = \frac{1 + q\beta K + q\beta K'}{K^2} + \frac{q\beta^2 K'}{K^2}$$

where: $K = Z^2 + \sigma\beta z + \varepsilon\beta z + \varepsilon\sigma\beta^2$

$K' = dK/dz = 2z + \sigma\beta + \varepsilon\beta$

With $Z_0 = 0.90$

$Z_1 = 0.8899$

$Z_2 = 0.8855$

$Z_3 = 0.8835$

$Z_4 = 0.8825$

⋮

$Z_7 = 0.8816$

$Z_8 = 0.8816$

$Z_9 = 0.8816$

converged!

$V = 1701.15$ cm^3/mol

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Problem 02: N_2 $\left\{\begin{array}{l} T = 175\ K \\ V = 3.75\times10^{-3}\ m^3/Kg \end{array}\right\}$ P?

(a) Ideal gas EOS

$$PV = RT \therefore P = RT/V$$

MW_{N_2}

$$P = 8.314\ \frac{J}{gmol.K} \times 175\ K \times \frac{1}{3.75\times10^{-3}\ m^3/Kg} \times \frac{1\ N.m}{1\ J} \times \frac{1\ gmol}{28\ g} \times \frac{1000\ g}{1\ Kg}$$

$[Pa = N/m^2]$ $\quad P = 1.386\times10^7\ Pa$

10000 KPa

$$\text{The error is } \frac{|P - P_{exp}|}{P_{exp}} \times 100 = \frac{|1.386\times10^7 - 10^7|}{10^7} \times 100$$

$\hookrightarrow$ 38.57%

(b) van der Waals ($T_c = 126.2\ K$; $P_c = 34\ bar = 34\times10^5\ Pa$)

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} = \frac{27}{64}\times\left(8.314\ \frac{m^3 Pa}{gmol\ K}\right)^2\times\frac{(126.2\ K)^2}{(3.4\times10^6\ Pa)}\times\left(\frac{1\ gmol}{28\ g}\times\frac{1000\ g}{1\ Kg}\right)^2$$

$[m^6.Pa/Kg^2]$ $\quad a = 174.23\ m^6\ Pa/Kg^2$

$$b = \frac{RT_c}{8P_c} = \frac{8.314}{8}\ \frac{m^3\ Pa}{gmol.K}\times\frac{1\ gmol}{28\ g}\times\frac{1000\ g}{1\ Kg}\times\frac{126.2\ K}{3.4\times10^6\ Pa}$$

$[m^3/Kg]$ $\quad b = 1.3777\times10^{-3}\ m^3/Kg$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$P = \left[8.314 \frac{m^3\,Pa}{\cancel{mol}.\cancel{K}} \times \frac{1\,\cancel{mol}}{28g} \times \frac{1000g}{1Kg} \times 175\,\cancel{K}\right]\left[3.75\times10^{-3}\frac{m^3}{Kg} - 1.3777\times10^{-3}\frac{m^3}{Kg}\right]^{-1} +$$

$$- 174.23 \frac{m^6\,Pa}{\cancel{Kg}^2} \times \frac{1}{(3.75\times10^{-3}\,m^3/\cancel{Kg})^2}$$

$$P = 51962.50 \frac{\cancel{m^3}\,Pa}{\cancel{Kg}} \times \frac{1}{2.372\times10^{-3}\,\cancel{m^3}/\cancel{Kg}} - 12389688.89\ Pa$$

$$P = 9.51\times10^6\ Pa$$

The error is 4.9%

(c) Benedict-Webb-Rubin EOS

If we just replace the given variables,

$$P = 10008.56\ KPa$$

The error is 0.09%