Quiz 8  
Chemical Engineering Thermodynamics  
March 4, 2021

In order to obtain an expression in the form of the virial expansion of $Z$, the van der Waals equation can be expanded using $1/(1-x) = 1 + x + x^2 + x^3 + \ldots$ for $-1 < x < 1$. The smaller $|x|$ the fewer terms are needed. (Fill in the table below with units. Show your work on separate sheets.)

(a) Do this expansion to obtain expressions for the second and third virial coefficients, $B$ and $C$ in terms of the van der Waals coefficients $a$ and $b$.

(b) For isopropanol vapor at 200°C the second and third virial coefficients are $B = -388$ cm$^3$/mole and $C = 26,000$ cm$^6$/mole$^2$. Calculate the van der Waals parameters $a$ and $b$ for isopropanol at 200 °C from these virial coefficients.

(c) A measure of the energy of attraction between atoms in the van der Waals model is $a/b$. How does this energy compare with $RT$ at 200 °C?

d) Obtain an estimate of the size of an ethanol molecule from $b$.

e) Compare the specific volume (cm$^3$/mole) of ethanol vapor at 200 °C and 1 MPa using:
   - the ideal gas law;
   - the virial equation to the second order (use Solver in Excel or quadratic formula);
   - the virial equation to the third order (use Solver in Excel);
   - the van der Waals equation using $T_c$, $P_c$ to calculate $a$ and $b$ (use Solver in Excel);
   - and the PREOS.xls program (using for a reference state an ideal gas at 298 K, 0.1 MPa, and using $H = 0$).

| a) | $B = b - \frac{a}{R}$ | $C = b^2$ |
| b) | $b = 161$ cm$^3$/mole | $a = 2,160,000$ cm$^6$/mole$^2$ MPa |
| c) | $a/b = 13.4$ K/mole | $RT = 393$ K/mole |
| d) | $r(\text{Å}) = 4.60$ | |
| e) | Ideal Gas | $V = 3,930$ cm$^3$/mole |
|      | Virial second order | $V = 3,490$ cm$^3$/mole |
|      | Virial third order | $V = 3,500$ cm$^3$/mole |
|      | van der Waals | $V = 3,620$ cm$^3$/mole |
|      | PREOS.xls | $V = 3,500$ cm$^3$/mole |
\( a \)

\[ p = \frac{RT}{V-b} - \frac{a}{V^2} \]

\[ Z = \frac{pV}{RT} = 1 + \frac{1}{V} \left( b - \frac{a}{RT} \right) + \frac{(b/a)^2}{V} + \frac{(b/a)^3}{V^2} + \ldots \]

\[ Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \text{ Van der Waals EOS} \]

\[ B = b - \frac{a}{RT} \quad C = b^2 \]

\( b \)

\[ b = \sqrt{C} = 161 \text{ cm}^3/\text{mol} \]

\[ a = RT(B - b) = -8.31 \text{ cm}^3/\text{mol} \text{ K} \cdot \frac{473 \text{ K}}{1388 \text{ cm}^3/\text{mol} - 161 \text{ cm}^3} \]

\[ a = \frac{2.16 \times 10^{-6} \text{ cm}^3}{\text{mol}^2} \]

\( c \)

\[ a/b = 13400 \text{ J} = 13.4 \text{ kJ/mol} \]

\[ RT = 8.31 \text{ cm}^3/\text{mol} \text{ K} \cdot 473 \text{ K} = 3909 \text{ kJ/mol} \]

\( d \)

\[ \frac{b}{N_A} = V = \frac{4\pi r^3}{3} = \frac{161 \text{ cm}^3/\text{mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} \]

\[ = 2.67 \text{ A}^3/\text{mol} \cdot \text{ul} \]

\[ r = \left( \frac{3(2.67 \text{ A}^3/\text{mol})}{4\pi} \right)^{1/3} = 4.00 \text{ A} \]
\[ z = \frac{PV}{RT} = 1 + \frac{B}{V} \]

\[ 0 = 1 + \frac{B}{V} - \frac{PV}{RT} \]

\[ 0 = 1 + \frac{386 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1} V}{V} \left( \frac{4.73 \text{ K}}{V} \right) \]

\[ V = 4,292 \text{ cm}^3 \text{ mol}^{-1} \]

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

\[ V = 4,292 \text{ cm}^3 \text{ mol}^{-1} \]

\[ V = 3,104 \text{ cm}^3 \text{ mol}^{-1} \]

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

\[ 0 = \frac{RT}{V-b} - \frac{a}{V^2} - P \]

\[ 0 = \frac{5.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 4.73 \text{ K}}{V} - \frac{840,000 \text{ cm}^6 \text{ mol}^{-2}}{V^2} - 1 \text{ MPa} \]

\[ T_c = 508 \text{ K} \]

\[ P_c = 4.76 \text{ MPa} \]

\[ a = \frac{27 R^2 T_c^2}{64 \left( \frac{1}{T_c} \right)} = 64 \left( \frac{8.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}}{4.76 \text{ K}} \right)^2 = 1580,000 \text{ cm}^6 \text{ mol}^{-2} \]

\[ b = \frac{RT_c}{8P} = \frac{8.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 508 \text{ K}}{8 \times 4.76 \text{ MPa}} = 887 \text{ cm}^3 \text{ mol}^{-1} \]

\[ V = 3,628 \text{ cm}^3 \text{ mol}^{-1} \]
\[ P = 0.5 \times 1 \text{ atm} \]

\[ V = 3.50 \theta \text{ cm}^3/\text{mol} \]

\[ z = \frac{PV}{RT} = 1 \]

\[ V = \frac{RT}{P} = \frac{8.31 \text{ cm}^3/\text{mol} \cdot \text{K}}{1 \text{ atm}} \]

\[ = 3930 \text{ cm}^3/\text{mol} \]