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).

Hicks
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a)	**B =** $b - \frac{a}{RT}$	**C =** b^2
b)	**b =** 161 cm^3/mol	**a =** 2,160,000 $\frac{cm^6}{mole^2}$ MPa
c)	**a/b =** 13.4 kJ/mole	**RT =** kJ/mole 3.93
d)	**r (Å) =** 4.00 Å	
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)

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\left(1-\frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$ van der Waals EOS

$$Z = \frac{PV}{RT} = 1 + \frac{1}{V}\left(b - \frac{a}{RT}\right) + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \ldots$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots$$ Virial EOS

$$\boxed{B = b - \frac{a}{RT} \qquad C = b^2}$$

(b)

$$b = \sqrt{C} = 161\ \text{cm}^3/\text{mole}$$

$$a = -RT(B-b) = -8.31\ \frac{\text{cm}^3\,\text{MPa}}{\text{K mole}}\ 473\,\text{K}\left(-398\ \frac{\text{cm}^3}{\text{mole}} - 161\ \frac{\text{cm}^3}{\text{mole}}\right)$$

$$a = \text{~~892,000~~}\ \text{~~2160,000~~}\ 2{,}160{,}000\ \frac{(\text{cm}^3)^2\,\text{MPa}}{(\text{mole})^2}$$

~~13.4~~

(c)

$$a/b = 13{,}400\ \text{J} = \text{~~13.4~~}\ 13.4\ \text{kJ/mole}$$

$$RT = 8.31\ \frac{\text{cm}^3\,\text{MPa}}{\text{K mole}}\ 473\,\text{K} = 3.93\ \text{kJ/mole}$$

(d)

$$\frac{b}{N_a} = V = \frac{4\pi r^3}{3} = \frac{161\ \text{cm}^3/\text{mole}\quad 1\times10^{24}\ \text{Å}^3/\text{cm}^3}{6.02\times10^{23}\ \text{molec/mole}}$$

$$= 267\ \text{Å}^3/\text{molecule}$$

$$r = \left(\frac{3(267\ \text{Å}^3/\text{molec})}{4\pi}\right)^{1/3} = 4.00\ \text{Å}$$

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

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

$$0 = 1 + \frac{-388 \frac{cm^3}{mol}}{V} - \frac{1\,MPa\,V}{8.31 \frac{MPa\,cm^3}{mol\,K}\,473K}$$

$V =$ ~~4,290~~ 3,494 cm^3/mol

$B = -388\ cm^3/mole$

$C = 26,000\ cm^6/mole^2$

$T = 473\ K$

$P = 1\ MPa$

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

$V =$ ~~4,290~~ cm^3/mol

3,504 $cm^3/mole$

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

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

$0 = \dfrac{8.31 \frac{cm^3\,MPa}{mol\,K}\,473K}{V -\ \text{~~161~~}\ cm^3/mol} - \dfrac{\text{~~892,000~~}\ \frac{cm^6\,MPa}{mole^2}}{V^2} - 1\,MPa$

$T_c = 508K$

$P_c = 4.76\,MPa$

$\omega = 0.669$

$a = \dfrac{27}{64}\dfrac{R^2 T_c^2}{P_c} = \dfrac{27}{64}\dfrac{\left(8.31 \frac{cm^3\,MPa}{mol\,K}\right)^2 (508K)^2}{4.76\,MPa} =$ 1,580,000 ~~146,300~~ $\dfrac{cm^6\,MPa}{mole^2}$

$b = \dfrac{RT_c}{8P_c} = \dfrac{8.31 \frac{cm^3\,MPa}{mol\,K}\,508K}{8\ 4.76\,MPa} = \dfrac{887}{8} \dfrac{cm^3}{mole} = 111 \dfrac{cm^3}{mole}$

$V =$ ~~4,540~~ 3,628 $cm^3/mole$

PREOS.xls

$V = 3{,}500\ cm^3/mole$

$$Z = \frac{PV}{RT} = 1$$

$$V = \frac{RT}{P} = \frac{8.31 \frac{cm^3 MPa}{mole K} (473 K)}{1 MPa}$$

$$= 3{,}930\ cm^3/mole$$