Homework Problem Set 3 Solutions

1. A bicycle tire was inflated to 9.3 bar total pressure in the cool of the morning when the temperature was 50°F. Later, the bicycle was used for a race on hot roads in the afternoon, when the temperature of the tire rose to 120°F. Assuming that the volume of the tire stayed the same and that the gases behave ideally, determine the pressure of the hot tire in psi.

The bicycle tire can be treated as a closed system, so the number of moles of air in the tire stays fixed. Since the volume also stays constant, we can solve for the ratio of $V/n$ using the ideal gas equation,

$$\frac{V}{n} = \frac{RT_1}{P_1},$$

where $T_1$ and $P_1$ are the temperature and pressure of the air in the tire in the morning. However, since $V/n$ remains fixed, we also have

$$\frac{V}{n} = \frac{RT_2}{P_2},$$

where $T_2$ and $P_2$ are the temperature and pressure of the air in the tire in the afternoon. Equating these two results, we have

$$\frac{RT_1}{P_1} = \frac{RT_2}{P_2}$$

The pressure $P_2$ is unknown and is what we want. Solving for $P_2$ leads to

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{(9.3 \text{ bar})(322.04 \text{ K})}{(283.15 \text{ K})} = 10.5 \text{ bar}.$$  

Converting to units of psi, we have

$$P_2 = 10.5 \text{ bar} \left(\frac{14.504 \text{ psi}}{1 \text{ bar}}\right) = 152.3 \text{ psi}.$$
2. Determine the pressure (in atm) exerted by 1 mole of methane placed into a bulb with a volume of 244.6 mL at 25°C. Carry out two calculations: in the first calculation, assume that methane behaves as an ideal gas; in the second calculation, assume that methane behaves as a real gas and obeys the van der Waals equation. [Hint: The van der Waals constant are available in your textbook.]

Part 1: Assuming that the gas obeys the ideal gas equation, we have

\[
P = \frac{nRT}{V} = \frac{(1 \text{ mol})(0.08205 \text{ L atm mol}^{-1} \text{K}^{-1})(298.15 \text{ K})}{0.2446 \text{ L}} = 100.0 \text{ atm}.
\]

Part 2: Note that the van der Waals coefficients \(a\) and \(b\) are available for a variety of gases including methane in the appendix of Engel & Reid (Table 7.4). Looking up the values of the constants \(a\) and \(b\), we find for methane that \(a = 2.303 \text{ L}^2 \text{atm mol}^{-2}\) and \(b = 0.0431 \text{ L/mol}\). Treating methane gas as obeying the van der Waals equation, we have

\[
P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{(1 \text{ mol})(0.08205 \text{ L atm mol}^{-1} \text{K}^{-1})(298.15 \text{ K})}{0.2446 \text{ L} - (1 \text{ mol})(0.0431 \text{ L mol}^{-1})} - \frac{(2.303 \text{ L}^2 \text{atm mol}^{-2})(1 \text{ mol})^2}{(0.2446 \text{ L})^2} = 82.9 \text{ atm}.
\]

Note that the pressure determined using the van der Waals equation is significantly lower than the pressure determined using the ideal gas equation. For methane, this is a regime where \(Z\) is significantly less than 1 as a result of van der Waals interactions.
3. The atmospheric surface pressure on Venus is 90 bar. The atmosphere near the surface is composed of 96% carbon dioxide and 4% other gases. Given a surface temperature of 730 K, what is the density of carbon dioxide present at the surface? Report the density in g/mL; assume ideal gas behavior.

The carbon dioxide partial pressure is related to the proportion of CO\(_2\) present (0.96) times the total pressure,

\[ P_{CO_2} = (0.96)(90 \text{ bar}) = 86.4 \text{ bar} . \]

The density \( d \) is defined as mass divided by volume,

\[ d = \frac{m}{V}, \]

where \( m \) is the mass and \( V \) is the volume. The mass \( m \) can be expressed in terms of the number of moles \( n \) and the molar mass \( M \),

\[ m = nM. \]

The number of moles \( n \) can be determined from the ideal gas equation. Solving this equation for \( n \) yields

\[ n = \frac{PV}{RT}. \]

This expression for the number of moles \( n \) can be substituted into the equation for the mass \( m \),

\[ m = nM, \]

or \[ m = \frac{PV}{RT}. \]

Finally, this equation for the mass \( m \) can be inserted into the relation for the density \( d \),

\[ d = \frac{m}{V}, \]

or \[ d = \frac{PM}{RT}. \]

Now, for the Venus atmosphere, the temperature is 730 K, the pressure of carbon dioxide is 86.4 bar, the molecular weight of CO\(_2\) is 44.0 g/mol, or 0.0440 kg/mol. Substituting into the expression for the density, the result is

\[
d = \frac{PM}{RT} = \frac{(86.4 \text{ bar})(44.0 \text{ g/mol})}{(0.08314 \text{ L bar mol}^{-1} \text{K}^{-1})(730 \text{ K})} = \frac{(62.64 \text{ g/L})}{\left(\frac{1\text{L}}{1000\text{cm}^3}\right)}
\]

\[ d = 0.06264 \text{ g/cm}^3 \text{ (or g/mL)}. \]
4. Determine the molar volume of propane at 660 K and 91 atm using (a) the ideal gas equation, and (b) the van der Waals equation. For part (b), the van der Waals constants of propane are $a = 9.39 \text{ L}^2\text{atm mol}^{-2}$ and $b = 0.0905 \text{ L/mol}$. In addition, you will need to solve a cubic equation, which you can do using a calculator, and online solver, or a spreadsheet.

Part a: The molar volume from the ideal gas equation is

$$V_m = \frac{RT}{P} = \frac{\left(0.08205 \text{ L atm mol}^{-1}\text{K}^{-1}\right)(660 \text{ K})}{(91 \text{ atm})} = 0.595 \text{ L/mol}.$$

Part b: Starting from the van der Waals equation,

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT,$$

we can obtain an equation for the molar volume. First, multiply both sides of the equation by $V_m^2$ to get

$$\left(PV_m^2 + a\right)(V_m - b) = RTV_m^2.$$

Then, multiply the terms on the left out and move everything to the left side to yield

$$PV_m^3 + aV_m - bPV_m^2 - ab - RTV_m^2 = 0.$$

Finally, we can divide by $P$ and collect terms to give

$$V_m^3 - \left(\frac{RT}{P} + b\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0.$$

Substituting numerical values and using the van der Waals coefficients, we have

$$\frac{RT}{P} + b = \frac{\left(0.08205 \text{ L atm mol}^{-1}\text{K}^{-1}\right)(660 \text{ K})}{91 \text{ atm}} + 0.0905 \text{ L mol}^{-1}$$

$$= 0.685588 \text{ L mol}^{-1},$$

$$\frac{a}{P} = \frac{9.39 \text{ L}^2\text{atm mol}^{-2}}{91 \text{ atm}}$$

$$= 0.103187 \text{ L}^2 \text{ mol}^{-2},$$

and

$$\frac{ab}{P} = \frac{\left(9.39 \text{ L}^2\text{atm mol}^{-2}\right)(0.0905 \text{ L mol}^{-1})}{91 \text{ atm}}$$

$$= 9.33841 \times 10^{-3} \text{ L}^3 \text{ mol}^{-3}.$$
4. Continued

These quantities yield the cubic equation

\[ V_m^3 - 0.68559 V_m^2 + 0.10319 V_m - 9.3384 \times 10^{-3} = 0. \]

This equation can be solved numerically, using a calculator for example, to obtain

\[ V_m = 0.522 \text{ L/mol}. \]

5. Use the virial equation (including the second virial coefficient only) to determine the pressure in atm of 1 mole of carbon dioxide gas contained in a volume of 5.0 L at 273 K. Compare your result to the pressure that would have been obtained from the ideal gas equation. [Hint: The second virial coefficient for carbon dioxide is available in your textbook.]

The virial equation is

\[ Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots \]

Using this equation but only including terms up to the second virial coefficient \( B \) (since that is all that your textbook includes), we can solve for the pressure,

\[ P = \frac{RT}{V_m} \left( 1 + \frac{B}{V_m} \right). \]

Substituting numerical values of \( T = 300 \text{ K} \) and \( V_m = 5.0 \text{ L/mol} \), and using the second virial coefficient for carbon dioxide from Engel & Reid Table 7.1 (\( B = -126 \text{ cm}^3/\text{mol} = -0.126 \text{ L/mol} \)), we have

\[ P = \frac{\left( 0.08205 \text{ L atm mol}^{-1} \text{K}^{-1}\right)(300 \text{ K})}{\left( 5.0 \text{ L mol}^{-1}\right)} \left[ 1 - \frac{0.126 \text{ L mol}^{-1}}{5.0 \text{ L mol}^{-1}} \right] \]

\[ P = 4.78 \text{ atm}. \]

Comparing this with the pressure from the ideal gas equation, we have

\[ P = \frac{RT}{V_m} \]

\[ = \frac{\left( 0.08205 \text{ L atm mol}^{-1} \text{K}^{-1}\right)(300 \text{ K})}{\left( 5.0 \text{ L mol}^{-1}\right)} \]

\[ P = 4.92 \text{ atm}. \]

So we see that the pressure of a real gas is somewhat lower than that of an ideal gas at moderate temperatures and pressures. This effect is due to the attractive interactions between real gas molecules that lower the pressure exerted by the molecules on the walls of the container.
6. By definition, the compression factor \( Z \) for an ideal gas equals 1. At room pressure and temperature, by approximately what percentage does this change for diatomic nitrogen upon inclusion of the second virial coefficient term? Recalculate this result for water vapor. At 300 K, the second virial coefficient \( B \) is \(-3.91 \text{ cm}^3/\text{mol}\) for diatomic nitrogen and \(-1126 \text{ cm}^3/\text{mol}\) for water vapor. [Hint: You will need to estimate the molar volume from the ideal gas equation in order to complete the calculations.]

The virial equation is

\[
Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots
\]

Including only the second virial coefficient \( B \), the expression becomes

\[
Z \approx \frac{PV_m}{RT} \approx 1 + \frac{B}{V_m}.
\]

The molar volume \( V_m \) may be estimated using the ideal gas equation,

\[
V_m = \frac{RT}{P}.
\]

At room temperature (300 K) and pressure (1 atm), the molar volume is

\[
V_m = \frac{RT}{P} = \frac{(0.08205 \text{ L atm mol}^{-1} \text{K}^{-1})(300 \text{ K})}{(1 \text{ atm})} = 24.62 \text{ L/mol}.
\]

Using this as an estimate for the molar volume, and substituting this into the virial expression along with \( B = -3.91 \text{ cm}^3/\text{mol} = -0.00391 \text{ L/mol} \), we have

\[
Z \approx 1 + \frac{B}{V_m} = 1 - \frac{0.00391 \text{ L/mol}}{24.62 \text{ L/mol}} = 1 - 0.00016
\]

\[
Z \approx 0.99984.
\]

So, our estimate is that diatomic nitrogen only deviates from the ideal case by about 0.02\% at 300 K and 1 atm pressure.
For water vapor, a similar calculation can be carried out. The approximate molar volume is identical, but the second virial coefficient for water vapor at 300 K is $B = -1126 \text{ cm}^3/\text{mol} = -1.126 \text{ L/mol}$. Substituting this into the expression for the compressibility leads to

\[
Z \approx 1 + \frac{B}{V_m} = 1 - \frac{1.126 \text{ L/mol}}{24.62 \text{ L/mol}} \approx 0.9543.
\]

From this result, we observe that water vapor deviates more than hydrogen from ideality. In the case of water vapor, the result is about 4.6% from the ideal case of 1 for the compression factor at 300 K and 1 atm. This is a deviation almost 300 times larger than that of diatomic nitrogen. This is a result of stronger intermolecular interactions between water molecules compared to the weaker interactions between nitrogen molecules.