

## APM 153 Assignment Nine – Using the van der Waals Equation to Calculate Pressure.

### Introduction

(1) The Ideal Gas Law ( $P = nRT/V$ ) calculates the pressure ( $P$ ) of a gas where

$P$  - pressure in Pascals                       $n$  - the amount of gas in moles  
 $T$  - is the temperature in °Kelvin         $V$  - is the volume (in cubic meters)  
 $R$  - is the universal gas constant (8.314 Joules/mole \* °K)

(2) The Ideal Gas Law however assumes that there is little or no interaction between gas molecules or between the gas molecules and the walls of the container.

(3) The van der Waals equation accounts for these interactions using two constants ( $a$  and  $b$ ). Each gas has its own values of  $a$  and  $b$  which have been derived empirically..

$$P = \frac{n * R * T}{V - n * b} - \frac{a * n^2}{V^2}$$

(4) For this week's assignment you are to set up the equations for both the Ideal Gas Law and the van der Waals equation and plot the resulting pressure for both equations for a range of temperatures and for three different gasses: propane, methane, and oxygen.

(5) The constants  $a$  and  $b$  for these gasses can be found in the table copied from the CRC Handbook of Chemistry and Physics. However, you will need to **convert the units**.

(6) For the constant  $a$ , you will need to first convert from  $\text{bar} \cdot \text{L}^2/\text{mol}^2$  to  $\text{Pa} \cdot \text{m}^6/\text{mol}^2$  and then convert the resulting value to  $\text{atm} \cdot \text{cm}^6/\text{mol}^2$ .

(7) For the constant  $b$ , you will need to convert from  $\text{L}/\text{mol}$  to  $0.001 \text{ m}^3/\text{mol}$  and then to  $\text{cm}^3/\text{mol}$ .

(8) To take propane as an example, the table lists the constant  $a$  as  $9.39 \text{ bar}/\text{L}^2/\text{mol}^2$ , but says in that one  $\text{bar}/\text{L}^2/\text{mol}^2$  is equal to  $0.1 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$ . So start with,..

$$\text{constant\_a} := 0.939 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$$

then type     $\text{constant\_a} =$

(9) When MathCad shows you the value of constant\_a, it also displays the “unit place keeper”. Type the units you want into the unit place keeper and MathCad automatically changes displays the value of constant\_a in the correct units.

(10) You can then assign the value of constant\_a being displayed to the variable a (used in the van der Waals equation) .

$$\text{for propane} \quad a := 9.267 * 10^6 \text{ atm*cm}^6/\text{mol}^2.$$

(11) You can set up the first section of your worksheet to perform these conversions and then just replace the initial values of a and b for each gas.

(12) Similarly, you can set up the equations once for the Ideal Gas Law and the van der Waals equation and when you change the values of a and b, the resulting plot will change as well.

(13) You will need to save the resulting plot for each gas before changing the values of a and b. See if you can come up with a way to save each plot.

(14) Finally, on the next page is an example of how your worksheet should look. Remember, MathCad is also a word processor and we will use only MathCad to print out our assignment. Your assignment will probably take three or more pages.

(15) The example worksheet also shows you how to set up both equations, but what you see is the result of entering the equations and assigning all the values using the correct syntax.

(16) For example, where I assign the range of temperature values to T, I typed in,...

T : 300, 301; 1700                      but MathCad converts this to                      T := 300,301.. 1700

(17) You will turn in one MathCad document showing your equations and with the plots showing pressure vs temperature for all three gasses.

(18) Assignment Nine will be due in class on Wednesday, April, 12<sup>th</sup>.

Joseph Cornell  
 APM 153  
 Assignment 10  
 April 7th, 2006

This assignment calculates the pressure of a given amount of propane in a container of a known volume using the van der Waals equation.

First, calculate the number of moles of gas given 22.7kg of propane (44 grams/mole)

$$n := 22.7 \frac{\text{kg}}{44 \frac{\text{gm}}{\text{mole}}}$$

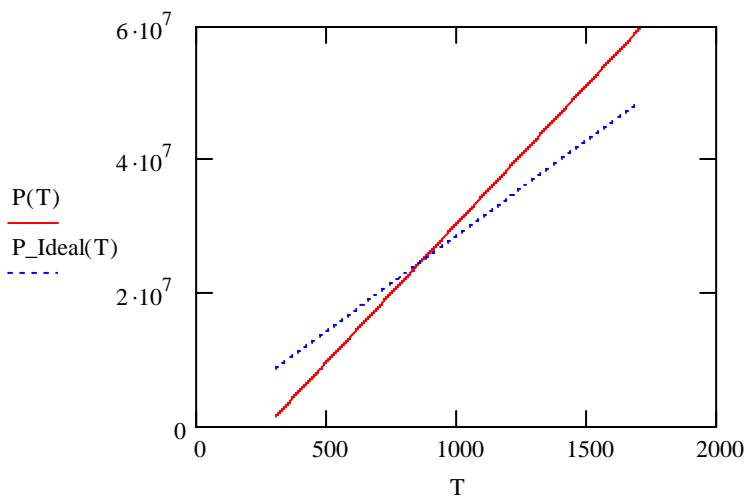
Next, assign the values for the volume, and the constants, R, a, and b

$$\underline{V} := 0.15 \text{m}^3 \quad \underline{R} := 8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}} \quad a := 9.267 \cdot 10^6 \text{atm} \cdot \frac{\text{cm}^6}{\text{mole}^2} \quad b := 90.5 \frac{\text{cm}^3}{\text{mole}}$$

Then, create the functions P(T) and P\_Ideal(T), and set T = a range from 300°K to 1700°K

$$P(T) := n \cdot R \cdot \frac{T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2} \quad P\_Ideal(T) := n \cdot R \cdot \frac{T}{V} \quad \underline{T} := 300\text{K}, 301\text{K}.. 1700\text{K}$$

Then, plot P(T) and P\_Ideal(T) to compare the results over the range of values for T



## VAN DER WAALS CONSTANTS FOR GASES

The van der Waals equation of state for a real gas is

$$(P + n^2a/V^2)(V - nb) = nRT$$

where  $P$  is the pressure,  $V$  the volume,  $T$  the temperature,  $n$  the amount of substance (in moles), and  $R$  the gas constant. The van der Waals constants  $a$  and  $b$  are characteristic of the substance and are independent of temperature. They are related to the critical temperature and pressure,  $T_c$  and  $P_c$ , by

$$a = 27R^2T_c^2/64P_c \quad b = RT_c/8P_c$$

This table gives values of  $a$  and  $b$  for some common gases. Most of the values have been calculated from the critical temperature and pressure values given in the table "Critical Constants" in this section. Van der Waals constants for other gases may easily be calculated from the data in that table.

To convert the van der Waals constants to SI units, note that 1 bar L<sup>2</sup>/mol<sup>2</sup> = 0.1 Pa m<sup>6</sup>/mol<sup>2</sup> and 1 L/mol = 0.001 m<sup>3</sup>/mol.

### REFERENCE

Reid, R.C., Prausnitz, J. M., and Poling, B.E., *The Properties of Gases and Liquids, Fourth Edition*, McGraw-Hill, New York, 1987.

Substance	$a$ bar L <sup>2</sup> /mol <sup>2</sup>	$b$ L/mol	Substance	$a$ bar L <sup>2</sup> /mol <sup>2</sup>	$b$ L/mol
Acetic acid	17.71	0.1065	Hydrogen sulfide	4.544	0.0434
Acetone	16.02	0.1124	Isobutane	13.32	0.1164
Acetylene	4.516	0.0522	Krypton	5.193	0.0106
Ammonia	4.225	0.0371	Methane	2.303	0.0431
Aniline	29.14	0.1486	Methanol	9.476	0.0659
Argon	1.355	0.0320	Methylamine	7.106	0.0588
Benzene	18.82	0.1193	Neon	0.208	0.0167
Bromine	9.75	0.0591	Neopentane	17.17	0.1411
Butane	13.89	0.1164	Nitric oxide	1.46	0.0289
1-Butanol	20.94	0.1326	Nitrogen	1.370	0.0387
2-Butanone	19.97	0.1326	Nitrogen dioxide	5.36	0.0443
Carbon dioxide	3.658	0.0429	Nitrogen trifluoride	3.58	0.0545
Carbon disulfide	11.25	0.0726	Nitrous oxide	3.852	0.0444
Carbon monoxide	1.472	0.0395	Octane	37.88	0.2374
Chlorine	6.343	0.0542	1-Octanol	44.71	0.2442
Chlorobenzene	25.80	0.1454	Oxygen	1.382	0.0319
Chloroethane	11.66	0.0903	Ozone	3.570	0.0487
Chloromethane	7.566	0.0648	Pentane	19.09	0.1449
Cyclohexane	21.92	0.1411	1-Pentanol	25.88	0.1568
Cyclopropane	8.34	0.0747	Phenol	22.93	0.1177
Decane	52.74	0.3043	Propane	9.39	0.0905
1-Decanol	59.51	0.3086	1-Propanol	16.26	0.1079
Diethyl ether	17.46	0.1333	2-Propanol	15.82	0.1109
Dimethyl ether	8.690	0.0774	Propene	8.442	0.0824
Dodecane	69.38	0.3758	Pyridine	19.77	0.1137
1-Dodecanol	75.70	0.3750	Pyrrole	18.82	0.1049
Ethane	5.580	0.0651	Silane	4.38	0.0579
Ethanol	12.56	0.0871	Sulfur dioxide	6.865	0.0568
Ethylene	4.612	0.0582	Sulfur hexafluoride	7.857	0.0879
Fluorine	1.171	0.0290	Tetrachloromethane	20.01	0.1281
Furan	12.74	0.0926	Tetrachlorosilane	20.96	0.1470
Helium	0.0346	0.0238	Tetrafluoroethylene	6.954	0.0809
Heptane	31.06	0.2049	Tetrafluoromethane	4.040	0.0633
1-Heptanol	38.17	0.2150	Tetrafluorosilane	5.259	0.0724
Hexane	24.84	0.1744	Tetrahydrofuran	16.39	0.1082
1-Hexanol	31.79	0.1856	Thiophene	17.21	0.1058
Hydrazine	8.46	0.0462	Toluene	24.86	0.1497
Hydrogen	0.2452	0.0265	1,1,1-Trichloroethane	20.15	0.1317
Hydrogen bromide	4.500	0.0442	Trichloromethane	15.34	0.1019
Hydrogen chloride	3.700	0.0406	Trifluoromethane	5.378	0.0640
Hydrogen cyanide	11.29	0.0881	Trimethylamine	13.37	0.1101
Hydrogen fluoride	9.565	0.0739	Water	5.537	0.0305
Hydrogen iodide	6.309	0.0530	Xenon	4.192	0.0516