Chem 4370 Spring 2017
Problem Set 1 Name: ______________________________

1. This is due on Tuesday, 24-Jan-2017 by the start of class. Late problem sets are not accepted.
2. All plots should be computer generated, plotted over an appropriate range, and clearly labeled.
3. Your final solution set should be neatly prepared. If I can't read it, it will be returned to you *ungraded*.
4. Use the NIST web-book to find the thermodynamic information you need. (webbook.nist.gov)
5. If you do come across old solutions sets, it's OK to use them for hints on how to do these problems and I highly suggest that you work together on these. *However*, the mid-term and final will be closed-book/closed-note/no-calculators.[1]

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1. (*10 points*) A certain gas obeys the van der Waals equation of state.

1. Show that for just one critical state specified by a critical temperature T_c and critical volume V_c that both
$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$
and
$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$
2. Write the equation of state giving $p = P/P_c$ in terms of $t = T/T_c$ and $v = V/V_c$. Make plots of p as a function of v for $t = 1/2$, $t = 1$, and $t = 2$.
3. Derive an expression for the isothermal compressibility, κ_T of a van der Waals gas in the reduced units. Make plots of κ_T vs. v at $t = 1/2$, $t = 1$, and $t = 2$.
4. Describe the physical state that results when there are three allowed values of v for a given p and t. For such a case, what is the sign of the isothermal compressibility at each of the 3 volumes. Are all 3 volumes physically acceptable and why (or why not)?

2. (*1 point*) Use the van der Waals equation to calculate the volume that 1.50mol of diethyl sulphide, $(C_2H_5)_2S$, would occupy at 114.0°C and 0.801 bar.

3. (*1 point*) 2.45 mol of ammonia fills a 7.00 liter bottle at 350 K. What does the ideal gas law predict the pressure to be? What does the van der Waals equation predict that the pressure will be? What is the isothermal compressibility of ammonia at 350K?

[1] I do allow slide rules if you have one and know how to use it.

4. (*1 point*) How much volume would 1.00 mole of CH_4 molecules take up if they were stacked on top of each other? How does this compare to the volume occupied by 1.00 mole of an ideal gas under STP conditions?

5. (*6 points*) The *Dieterici equation of state* is given by

$$P = \frac{RT}{\bar{V} - b} e^{-a/(\bar{V}RT)}.$$

This can be written as a virial expression in terms of the pressure.[2]

$$P\bar{V} = A_p + B_p P + C_p P^2 + \cdots$$

1. Determine the A_p, B_p and C_p coefficients in the virial expansion.
2. Evaluate the a and b constants in the Dieterici equation in terms of the critical pressure and temperature.
3. Determine a reduced form of the equation of state.

6. (*5 points*) Use a numerical software package such as MathCad or Mathematica to evaluate the integral

$$S = 4\pi^{1/2} \left(\frac{2\alpha}{\pi}\right)^{3/4} \int_0^\infty r^2 e^{-r} e^{-\alpha r^2} dr$$

for values of α between 0.2 and 0.3. Show that S has a maximum at $\alpha = 0.271$. I suggest performing the integral numerically for given values of α and plotting the final results. [3]

7. (*6 points*) Use the van der Waals equation of state to plot the compressibility factor Z against P for methane for the following temperatures: 180K, 189K, 190K, 200K, and 250K. Hint: calculate Z as a function of $\overline{V}$ and then P as a function of $\overline{V}$, and then plot Z vs. P over the range of 0 to 500 bar. I suggest using either Excel or Mathematica to do this problem since you can not obtain an algebraic formula for $Z(P)$.

[2] Hint: at low pressure you can use the ideal gas law for $\bar{V}$ in the exponent, then perform a Taylor expansion in terms of p.

[3] The integral can be performed by hand and requires the use of special functions (Error function, or Erf) which you may have not seen before. The result reads:

$$S = \frac{\sqrt{\pi} e^{\frac{1}{4\alpha}} (2\alpha + 1) \text{Erfc}\left(\frac{1}{2\sqrt{\alpha}}\right) - 2\sqrt{\alpha}}{8\alpha^{5/2}}$$

where Erfc(z) is the complimentary error function which you can read about on Wikipedia.