Problem Set 2: Equations of State - Properties of Gases

HCHE 321L: Physical Chemistry 1

Due Date: September 1st, 2017

Problem 1

Consider a gas that deviates from ideal behavior only slightly, such that it can be defined by the following equation of state:

$$P(V-b) = nRT$$

Prove that this equation satifies the following relationship:

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Problem 2

As gases are compressed at extremely high pressures and cooled, they condense to form liquids. This phenomena can NOT be explained via the ideal as equation, however can be modeled in the Van der Waals equation! At high pressure, the van der Waals equation can be rearranged into the following cubic equation:

$$\bar{V} = b + \frac{P}{a}\left(b + \frac{RT}{P}\right)\bar{V}^2 - \left(\frac{P}{a}\right)\bar{V}^3$$

where $\bar{V}$ is the molar volume $\bar{V} = V/n$ If we drop the quadratic and cubic terms, then we obtain $\bar{V}_o = b$ as a first approximation to the smallest root of the equation. This would represent the volume of the liquid form.

a) Using this approximate value of $\bar{V}$ in the higher terms, show that the next approximation for the volume of the liquid is:

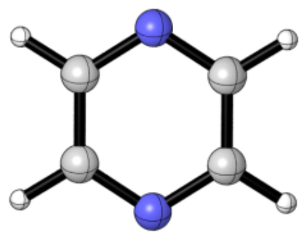
$$\bar{V} = b + \frac{b^2 RT}{a}$$

b) From the expression in part a), show that the first approximation for the thermal expansion coefficient α can be expressed as

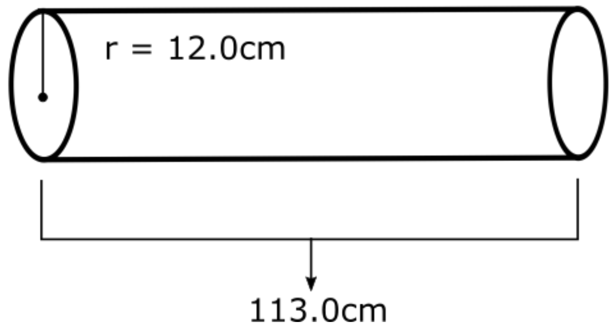
$$\alpha = \frac{bR}{a}$$

Problem 3

A 113.0cm cylindrical tube with radius 12.0cm is filled with 500g of pyrazine ($C_4N_2H_4$) gas. Calculate the following considering this gas at 27°C



$C_4N_2H_4$



a) The root mean square velocity of pyrazine molecules.

b) The pressure using the ideal gas law.

c) The pressure using Van der Waal's equation (the VDW constants for pyrazine are $a = 19.77$bar L^2 mol^{-2} and $b = 0.1137$ L mol^{-1})

Problem 4

For most liquids and solids at ordinary temperature and pressure an approximate equation of state is

$$\bar{V} = c_1 + c_2T + c_3T^2 - c_4P - c_5PT$$

where $c_1, ..., c_5$ are positive constants that must be evaluated by fitting observed $\bar{V}$ vs. T and P data. For a liquid obeying this equation of state, find expressions for the *thermal expansion coefficient*(α) and *isothermal compressibility coefficient*(κ).

Problem 5

Recall that the *total differential* of a general function $f(x, y, z)$ can be expressed as:

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

Answer the following questions assuming an ideal gas:

a) Show that the *total differential* can be expressed as:

$$dP = P\left[\frac{1}{n}dn + \frac{1}{T}dT - \frac{1}{V}dV\right]$$

b) Suppose 1.0000 mole of an ideal gas at 300.00K in a 30.000L vessel has its temperature increased by 1.00K and its volume increased by 0.050L. Use the result of part a) to estimate the total change in pressure, ΔP.

c) Calculate ΔP exactly for the change in part b) and compare it with the estimate given by dP

Problem 6

A mixture of N_2 and O_2 has a density of 1.185g/L at 25°C and 101.3kPa. Find the mole fraction of O_2 in the mixture.