

Midterm Examination 1

1. A goat weighing 20 kg produces about 375 cm³ gas per hour in his intestines. Assume that the gas is Methane; CH₄ with M = 16 g/mol. How long does it take the goat to produce an amount of intestinal gas equal to his own weight? Take T = 310K. (*Problem shamelessly stolen from the Bromberg text.*)

$$\begin{aligned}n &= PV/RT = (1 \text{ atm}) (0.375 \text{ L}) / (0.08206 \text{ Latm/Kmole})(310 \text{ K}) \\ &= 0.0147 \text{ mole / hour}\end{aligned}$$

$$\text{mass} = 0.0147 \text{ mole} (16 \text{ g/mole}) = 0.23 \text{ g / hour}$$

$$\text{time} = 20,000\text{g} / (0.236 \text{ g / hour}) = 84795 \text{ hours} = 9.7 \text{ years}$$

2. In 1894, Sir William Ramsey and Lord Rayleigh isolated a gaseous element present in Air by removing from an Air sample all the Nitrogen, Oxygen, Carbon Dioxide and Water Vapor. The resulting gas residue had a density of 1.63 g/L at 25°C and 1 atm. What is the Atomic Weight of this element?

$$P = (n/V) RT = (m/V) RT/M = \rho RT / M$$

So,

$$\begin{aligned}M &= \rho RT / P = (1.63 \text{ g/L}) (0.08206 \text{ L atm/K mole})(298 \text{ K}) / (1 \text{ atm}) \\ &= 39.8 \text{ g/mole (Argon)}\end{aligned}$$

3. The Virial Equation of State for Methane at 200 K is:

$$Z = 1 - 0.00574 P + (6.86 \times 10^{-6}) P^2 + (18.0 \times 10^{-9}) P^3$$

We have noted that the Virial Expansion for a van der Waals gas is:

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

Suppose Methane behaves as a van der Waals gas with:

$$a = 2.273 \text{ L}^2 \text{ atm/mol}^2$$

$$b = 0.0431 \text{ L/mol}$$

- a) Calculate the 2nd Virial Coefficient at 200K for Methane assuming it behaves as a van der Waals gas.

$$\begin{aligned} B' &= 1/RT (b - a/RT) = 1/(0.08206)(200) (0.0431 - 2.273/(0.08206)(200)) \\ &= -0.00581 \text{ atm}^{-1} \end{aligned}$$

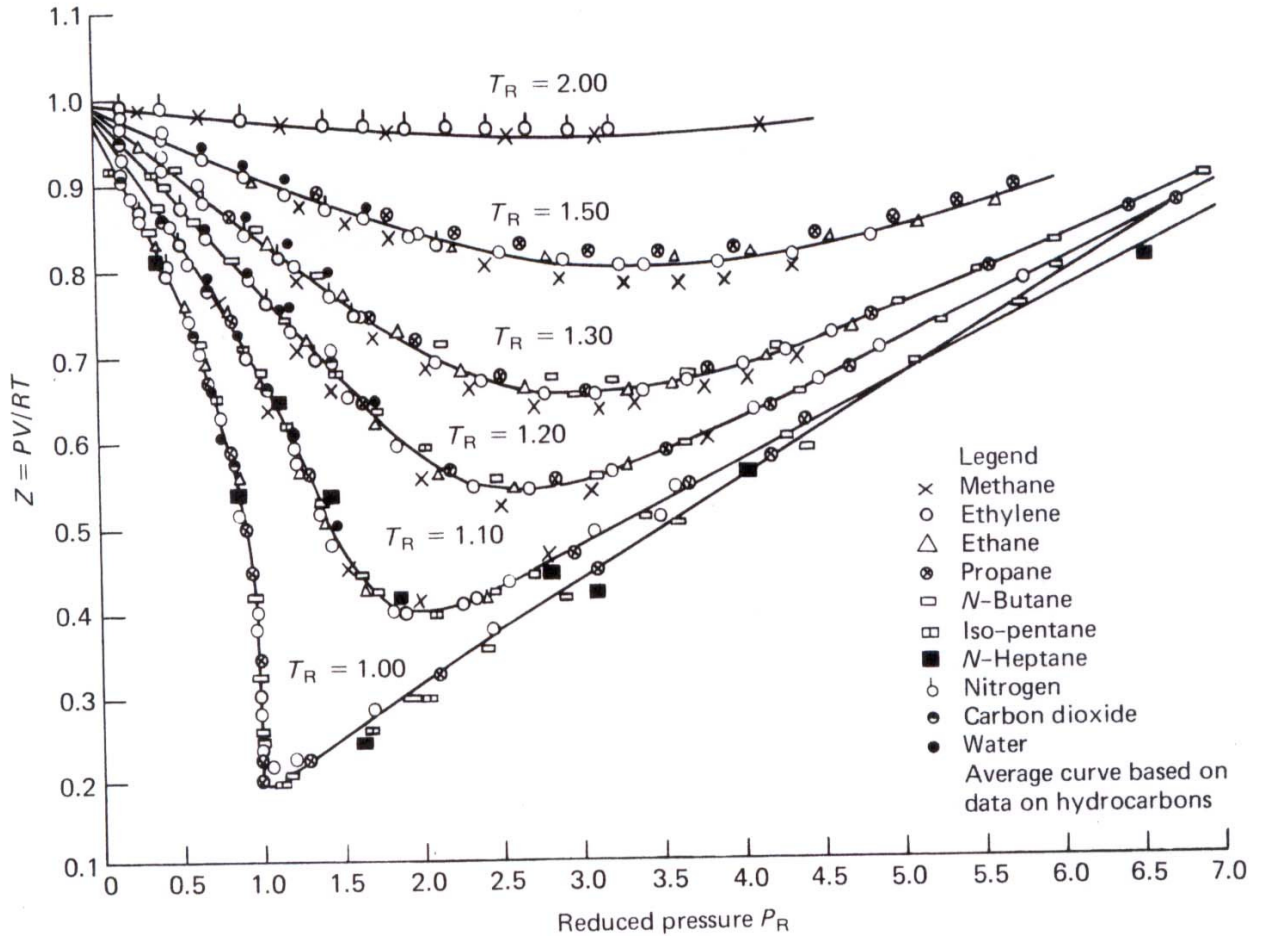
- b) What are some of the problems associated with this calculation?

Beyond the fact that the van der Waals equation of state is not very good at quantitatively predicting the properties of gases, we do not know how the constants a and b are determined. These constants actually vary with temperature and may not have been calculated from data that will represent the current conditions well.

- c) Calculate the percentage error introduced into the 2nd Virial Coefficient by assuming Methane exhibits van der Waals gas behavior.

$$\% \text{ Error} = (0.00574 - 0.00581) / 0.00574 \times 100 = 1.2\%$$

4. The Compressibility Factor for a number of gases as a function of the reduced state variables is given as:



- a) Use this data to determine the Molar Volume of CO_2 at 91.8°C and **145.6 atm**. Critical Constants for Carbon Dioxide are:

$$\begin{aligned} T_c &= 304.16 \text{ K} \\ P_c &= 72.83 \text{ atm} \\ V_c &= 94.23 \text{ cm}^3/\text{mole} \end{aligned}$$

$$T_r = T/T_c = 364.95 / 304.16 = 1.2$$

$$P_r = P/P_c = 145.6 / 72.83 = 2.0$$

From the chart, $Z \sim 0.58$

$$\text{So, } \bar{V} = ZRT/P = (0.58)(0.08206)(364.95)/(145.6) = 0.119 \text{ L/mole}$$

- b) Calculate the Molar Volume of CO₂, under these conditions, assuming the gas behaves Ideally. What is the percentage difference between these two calculations?

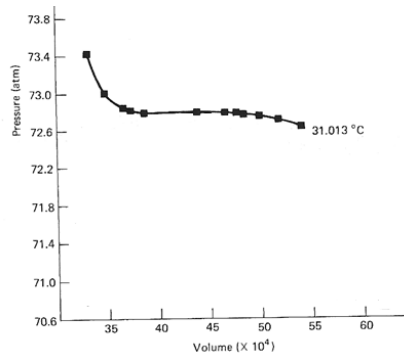
$$\bar{V} = RT / P = (0.08206) (364.95) / (145.6) = 0.2056 \text{ L/mole}$$

$$\% \text{ diff} = (0.119 - 0.2056) / (0.1623) \times 100 = 53\%$$

- c) Comment on the quality of the calculation in part (a).

The calculation using the estimated value for Z is probably pretty good. CO₂ is a non-polar gas, like most of the gases used to generate the chart. Also, some data for CO₂ is used to generate the chart.

- d) The critical isotherm for CO₂ is as plotted below:



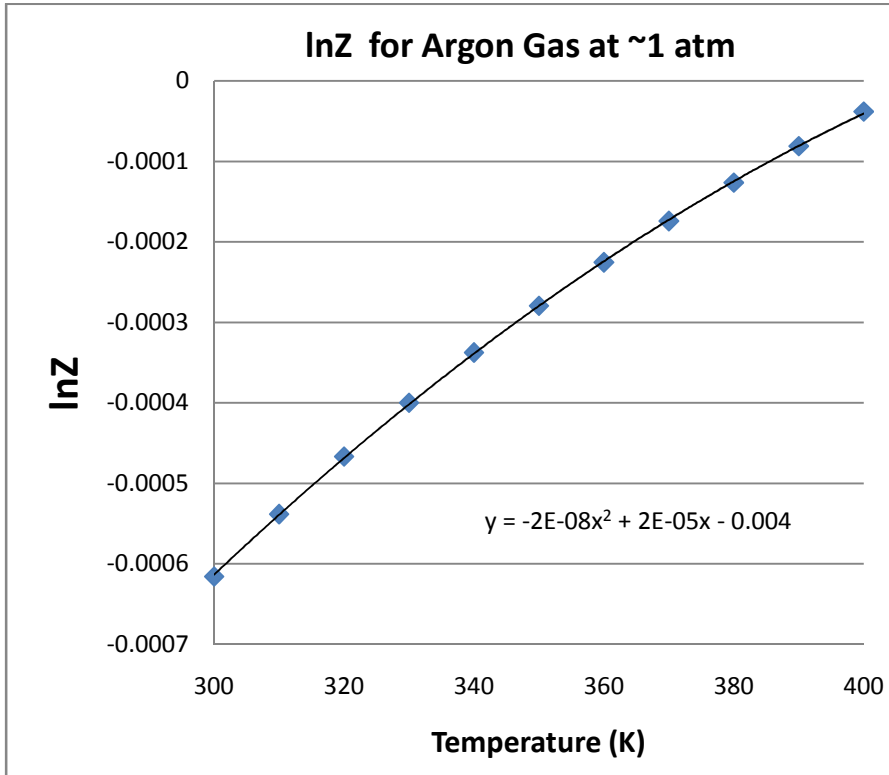
Based on the form of this isotherm, explain why the curve for $T_R = 1.00$ in the above Z vs. P_R diagram is nearly vertical below $P_R \sim 1.00$.

Near the critical point, changes in \bar{V} do not cause significant changes in P. In other words, the isotherm is fairly flat. Hence, when $P_r \sim 1$, the Z vs. P_r curve will show sharp increases in Z.

5. We have found that the Thermal Compressibility α depends on the Compressibility Factor Z as:

$$T \alpha = 1 + T \left(\frac{\partial \ln Z}{\partial T} \right)_P$$

A plot of $\ln Z$ vs T for Argon gas at approximately 1 atmosphere pressure gives:



Calculate α for Argon at 1 atm and 273.15 K.

$$\left(\frac{\partial \ln Z}{\partial T} \right)_P = 2 \times 10^{-5} - (4 \times 10^{-8}) T \sim 2 \times 10^{-5} - (4 \times 10^{-8}) (273.15) = 9.1 \times 10^{-6} \text{ K}^{-1}$$

$$T \alpha = 1 + T \left(\frac{\partial \ln Z}{\partial T} \right)_P = 1 + (273.15) (9.1 \times 10^{-6}) = 1.002$$

$$\alpha = 1.002 / 273.15 = 0.0037 \text{ K}^{-1}$$

6. Suppose that you have data giving the Compressibility Factor (Z) for a gas as a function of Temperature and Concentration (c); $c = 1/\bar{V}$.

a) Derive an expression for calculating $\left(\frac{\partial P}{\partial c}\right)_T$ from this data.

$$Z(T,c) = P / cRT$$

$$\text{So, } P = cRTZ$$

$$\left(\frac{\partial P}{\partial c}\right)_T = ZRT + cRT \left(\frac{\partial Z}{\partial c}\right)_T$$

b) What is this result for an Ideal Gas?

$$Z = 1 \quad \text{and} \quad \left(\frac{\partial Z}{\partial c}\right)_T = 0$$

So,

$$\left(\frac{\partial P}{\partial c}\right)_T = (1) RT + cRT (0) = RT$$

7. The Isothermal Compression Factor for Copper is $\kappa = 7.35 \times 10^{-7} \text{ atm}^{-1}$ at 273K. Recall:

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

What is the fractional decrease in the volume $\Delta V/V$ of a Copper sample if the pressure on it is increased by 1000 atm under constant temperature conditions? Hint: The total volume will change only slightly.

$$\Delta V / V \sim \kappa \Delta P = -(7.35 \times 10^{-7} \text{ atm}^{-1}) (1000 \text{ atm}) = -7.35 \times 10^{-4} \sim 0.0735\%$$