

Department of Chemistry, Oregon State University
Physical Chemistry Assignment 1
due: 10 October 2014, 9 AM

1. At $98^\circ F$ (body temperature) water exists as a gas and a liquid with a vapor pressure of 47 torr. a) calculate the number density and molar density of gaseous water; and b) calculate the packing fraction of gas phase water. The liquid phase has $\eta \simeq 0.4$. Assume that a water molecule is spherical with a diameter of 3.0\AA . Packing fraction: $\eta \equiv (\text{volume per particle}) * \text{number of particles per unit volume}$.
2. Write the van der Waals equation for P in terms of the molar density, $\rho = n/V$ and T . Next, apply the conditions of criticality to derive the critical constants a and b in terms of T_c , and ρ_c .
3. At a pressure of 200 bar and a temperature of 200K, the ideal gas equation may not be quantitative for water vapor. Consult your textbook for water's van der Waals a and b parameters and calculate the first non-ideal correction to Z , i.e., $B_2(T)\rho$.
4. Show that

$$\alpha_P = - \left(\frac{\partial \ln \rho}{\partial T} \right)_P \quad (1)$$

$$\kappa_T = \left(\frac{\partial \ln \rho}{\partial P} \right)_T \quad (2)$$

5. Derive α_P , the thermal expansion coefficient, and κ_T , the isothermal compressibility, for a gas obeying

$$Z(\rho, T) = 1 + B_2\rho + B_3\rho^2 \quad (3)$$

where B_2 and B_3 are independent of T .

6. What is the atmospheric pressure (in bar) at an elevation of 10 km (at the so-called tropopause) assuming the barometric distribution law and a lapse rate (decrease in T with altitude) of 7 K/km. At ground level, $T = 300K$ and $P = 1$ bar.

Assignment 1.

$$1. \quad P = 47 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times 1.01325 \frac{\text{bar}}{\text{atm}} = 0.0627 \text{ bar}$$

$$T = 98^\circ\text{F}, \quad T(^{\circ}\text{C}) = (98 - 32) \times \frac{100}{180} = 36.7^\circ\text{C}$$

$$PV = nRT, \quad \rho = \frac{n}{V} = \frac{P}{RT}$$

$$\rho = 0.0627 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \left/ \left[(273.15 + 36.7) \text{ K} \cdot 8.315 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right] \right.$$

$$a) \quad \rho = 2.43 \text{ moles/m}^3 \quad \text{or} \quad \rho = 2.43 \times 10^{-6} \frac{\text{moles}}{\text{L}}$$

packing fraction

$$\eta = \left(2.43 \times 10^0 \frac{\text{moles}}{\text{m}^3} \right) \times \frac{\pi \left(3 \times 10^{-10} \text{ m} \right)^3}{6} \cdot 6.022 \times 10^{23}$$

$$b) \quad \eta = \frac{2.43 \times 10^{-5}}{2.07} \text{ in the vapor phase, } \eta = 0.40 \text{ liquid phase}$$

2. van der Waals

$$P = \frac{\rho RT}{1 - b\rho} - a\rho^2$$

$$\text{At the critical pt, } \left(\frac{\partial P}{\partial \rho} \right)_T = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_T = 0$$

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \frac{RT}{1 - b\rho} + \frac{\rho RT}{(1 - b\rho)^2} b - 2a\rho$$

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \frac{RT}{(1 - b\rho)^2} (1 - b\rho + b\rho) - 2a\rho = \frac{RT}{(1 - b\rho)^2} - 2a\rho \quad (1)$$

$$\left(\frac{\partial^2 P}{\partial \rho^2} \right)_T = \frac{2RT}{(1 - b\rho)^3} b - 2a \quad (2)$$

Multiple Eq(2) by p and subtract it from Eq(1)

$$\frac{RT}{(1-bp)^2} - 2ap - \left\{ \frac{2RT bp}{(1-bp)^3} - 2ap \right\}$$

$$= \frac{RT}{(1-bp)^2} \left\{ \frac{1-2bp}{1-bp} \right\} = \frac{RT}{(1-bp)^2} [1-3bp] = 0$$

$$\therefore 3bp = 1 \text{ and } bp_c = 1/3$$

Next substitute $bp = 1/3$ into

$$\frac{RT}{(1-bp)^2} = 2ap \Rightarrow \frac{RT}{(1-\frac{1}{3})^2} = \frac{2a}{3b}$$

$$RT_c = \frac{2}{3} \left(\frac{a}{b} \right) \cdot \frac{4}{9} = \frac{8}{27} \frac{a}{b}$$

$$\therefore b = \frac{1}{3p_c}, \quad a = RT_c \left(\frac{27b}{8} \right) = \frac{9}{8} \frac{RT_c}{p_c}$$

3.

$$\text{For H}_2\text{O, } a = 5.536 \frac{\text{L}^2 \cdot \text{bar}}{\text{mol}^2}$$

$$b = 0.030 \frac{\text{L}}{\text{mol}}$$

$$B_2p = \left(b - \frac{a}{RT} \right) \frac{p}{RT} = \left[\frac{0.030 \frac{\text{L}}{\text{mol}} - 5.536 \frac{\text{L}^2 \cdot \text{bar}}{\text{mol}^2}}{(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}) (200\text{K})} \right]$$

$$\times \left[\frac{200 \text{ bar}}{(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}) 200\text{K}} \right]$$

$$B_2p = -3.64$$

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@ these conditions.

$$4. \quad \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial \ln V}{\partial T} \right)_p = - \left(\frac{\partial \ln p}{\partial T} \right)_p$$

$$\text{since } \ln V = \ln(n/p) = \ln n - \ln p$$

Likewise,

$$\kappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = - \left(\frac{\partial \ln V}{\partial p} \right)_T = \left(\frac{\partial \ln p}{\partial p} \right)_T$$

5.

$$Z = 1 + B_2 p + B_3 p^2, \quad p = pRT \cdot Z = RT \{ p + B_2 p^2 + B_3 p^3 \}$$

$$dp = \left(\frac{\partial p}{\partial p} \right)_T dp + \left(\frac{\partial p}{\partial T} \right)_p dT = RT [1 + 2B_2 p + 3B_3 p^2] dp + R p [1 + B_2 p + B_3 p^2] dT$$

$$\alpha_p = - \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_p = \frac{1}{p} \underbrace{\left(\frac{\partial p}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_p}_{\text{cyclic rule}} = \frac{R p [1 + B_2 p + B_3 p^2]}{p \cdot RT [1 + 2B_2 p + 3B_3 p^2]}$$

$$\alpha_p = \frac{1}{T} \frac{[1 + B_2 p + B_3 p^2]}{[1 + 2B_2 p + 3B_3 p^2]}$$

next

$$\kappa_T = \left(\frac{\partial \ln p}{\partial p} \right)_T = \frac{1}{p} \left(\frac{\partial p}{\partial p} \right)_T = \frac{1}{p \cdot RT [1 + 2B_2 p + 3B_3 p^2]}$$

$$\kappa_T = \frac{1}{p [1 + 2B_2 p + 3B_3 p^2]}$$

6. The barometric law is

$$P = P_0 \exp(-mgh/RT)$$

$$m = \frac{29 \text{ g}}{\text{mole}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} =$$

$$h = 10 \text{ km} = 10^4 \text{ m}, \quad T = 300 \text{ K} - \frac{7 \text{ K}}{\text{km}} \times 10 \text{ km}$$

$$T = 230 \text{ K}$$

$$R = 8.315 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$P = 1 \text{ bar} \times \exp\left(-\frac{29 \times 10^{-3} \text{ kg}^{\text{mol}} \cdot 9.8 \frac{\text{m}}{\text{s}^2} \cdot 10^4 \text{ m}}{(230 \text{ K}) \left(8.315 \frac{\text{J}}{\text{K} \cdot \text{mol}}\right)}\right)$$

$$P \approx 0.226 \text{ bar}$$