

CHM 3400 – Problem Set 1

Due date: Wednesday, January 15<sup>th</sup>.

Do all of the following problems. Show your work. Note the following constants and conversion factors.

$$\begin{array}{ll}
 1 \text{ L} = 1 \text{ dm}^3 = 1000 \text{ cm}^3 = 1000 \text{ mL (exact)} & R = 0.082057 \text{ L}\cdot\text{atm/mol}\cdot\text{K} \\
 1 \text{ m}^3 = 1000 \text{ L (exact)} & R = 8.3145 \text{ J/mol}\cdot\text{K} \\
 1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ torr (exact)} & k = 1.3806 \times 10^{-23} \text{ J/K} \\
 1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ Nt/m}^2 \text{ (exact)} & N_A = 6.0221 \times 10^{23} \text{ molecule/mol}
 \end{array}$$

"Jumpin' Jack Flash, it's a gas gas gas" – Mick Jagger, Keith Richards

1) For Mars, the pressure and temperature of the atmosphere at surface level is  $p = 610. \text{ Nt/m}^2 = 610. \text{ Pa}$ , and  $T = 215. \text{ K}$ . Under these conditions we can assume the ideal gas law applies.

a) What is the molar density of the Martian atmosphere at the surface of Mars? Give your final answer in units of  $\text{mol/m}^3$ .

b) The number density of molecules in a gas ( $\rho_N$ ) is defined as

$$\rho_N = \frac{N}{V} = \frac{\text{number of molecules}}{\text{volume}} \quad (1.1)$$

$\rho_N$  represents the number of gas molecules per unit volume of the gas.  $\rho_N$  is usually given in units of  $\text{molecules/cm}^3$ , although other units can be used.

Based on your answer to part a, find  $\rho_N$  for the atmosphere of Mars at the surface of the planet. Give your final answer in units of  $\text{molecules/cm}^3$ .

c) The atmosphere of Mars is to a first approximation a mixture of carbon dioxide, nitrogen, and argon, with trace amounts of other gases. If we ignore the trace gases, the mole fractions of  $\text{CO}_2$ ,  $\text{N}_2$ , and Ar in the atmosphere of Mars are (along with the molecular masses)

$$\begin{array}{lll}
 X_{\text{CO}_2} = 0.955 & X_{\text{N}_2} = 0.026 & X_{\text{Ar}} = 0.019 \\
 M_{\text{CO}_2} = 44.01 \text{ g/mol} & M_{\text{N}_2} = 28.01 \text{ g/mol} & M_{\text{Ar}} = 39.95 \text{ g/mol}
 \end{array}$$

Based on your answer to part a and the information above (and assuming Dalton's Law is correct), find the density by mass of the Martian atmosphere at surface level. Give your final answer in units of  $\text{g/m}^3$ . (Note that density by mass for a gas is often given in units of  $\text{kg/m}^3$ . We use units of  $\text{g/m}^3$  here because of the low value for density compared to that for the sea level density of the Earth's atmosphere.)

2) The element chlorine has two naturally occurring isotopes,  $^{35}\text{Cl}$  ( $m = 34.969 \text{ amu}$ ) and  $^{37}\text{Cl}$  ( $m = 36.965 \text{ amu}$ ). The density of a sample of chlorine gas ( $\text{Cl}_2$ ), measured at  $p = 1.0000 \text{ torr}$ ,  $T = 273.15 \text{ K}$ , is  $D = 4.168 \times 10^{-3} \text{ g/L}$ . Assuming that chlorine gas obeys the ideal gas law, find the percent by number (related to the mole fraction) of chlorine atoms that are the  $^{35}\text{Cl}$  isotope, and the percent that are the  $^{37}\text{Cl}$  isotope.

3) A 1.640 L gas cylinder contains 158.3 g of carbon monoxide ( $\text{CO}$ ,  $MW = 28.01 \text{ g/mol}$ ) at a temperature  $T = 22.0 \text{ }^\circ\text{C}$ . Find the following

a) The value for pressure for the gas, using the ideal gas law. Give your final answer in units of atm.

b) The value for pressure for the gas, using the van der Waals equation, For  $\text{CO}$ ,  $a = 1.453 \text{ L}^2\cdot\text{atm/mol}^2$ ,  $b = 0.0395 \text{ L/mol}$ . Give your final answer in units of atm.

c) Which value for pressure do you expect to be closer to the actual pressure of carbon monoxide in the gas cylinder? Why?

4) The values for the critical pressure ( $p_c$ ), critical molar volume ( $V_{m,c}$ ) and critical temperature ( $T_c$ ) for a gas can be estimated from the van der Waals  $a$  and  $b$  coefficients using the relationships

$$p_c = \frac{a}{27b^2} \qquad V_{m,c} = 3b \qquad T_c = \frac{8a}{27bR} \qquad (4.1)$$

a) What is the physical significance of  $T_c$ , the critical temperature, for a real gas?

b) Using the relationships in eqn 4.1, find the values for  $p_c$ ,  $V_{m,c}$ , and  $T_c$  for carbon monoxide (Note that values for the van der Waals coefficients for carbon monoxide are given in problem 3). Give your final answers in units of atm (for  $p_c$ ),  $\text{cm}^3/\text{mol}$  (for  $V_{m,c}$ ) and K (for  $T_c$ ).

c) The experimental values for the critical constants for carbon monoxide are  $p_c = 34.6$  atm,  $V_{m,c} = 93.0$   $\text{cm}^3/\text{mol}$ , and  $T_c = 134.4$  K. How well do the values found using eqn 4.1 agree with the experimental values for the critical constants.

5) The collision cross section for an air molecule is  $\sigma = 0.42$   $\text{nm}^2$ . Use  $MW = 29.0$  g/mol for the molecular mass of an air molecule. Find the following for a sample of air at  $p = 1.00$  atm and  $T = 288$ . K.

a)  $d$ , the diameter of an air molecule (which corresponds to the size of an air molecule). Use the relationship  $\sigma = \pi d^2$ . Give your final answer in units of nm.

b)  $v_{\text{rms}}$ , the root mean square average speed of a molecule of air in the sample, given by the equation

$$v_{\text{rms}} = (3RT/M)^{1/2} \qquad (5.1)$$

Give your final answer in units of m/s.

c)  $\lambda$ , the mean free path of an air molecule, which represents the average distance the molecule travels between collisions.  $\lambda$  is given by the relationship

$$\lambda = \frac{kT}{2^{1/2}\sigma p} \qquad (5.2)$$

Give your final answer in units of nm.

d)  $z$ , the average number of collisions for a molecule of air, given by the relationship

$$z = \frac{2\sigma p}{kT} (8RT/\pi M)^{1/2} \qquad (5.3)$$

Give your final answer in units of collisions/s.

### Solutions.

1) a) Molar density is the number of moles per unit volume. Since

$$pV = nRT$$

$$\text{then } \frac{n}{V} = \frac{p}{RT} = \frac{(610. \text{ Pa}) (1. \text{ atm}/1.013 \times 10^5 \text{ Pa})}{(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (215. \text{ K})} = \frac{3.41 \times 10^{-4} \text{ mol}}{\text{L}} \frac{1000 \text{ L}}{\text{m}^3} = 0.341 \text{ mol}/\text{m}^3$$

b) Number density is the number of molecules per unit volume.

$$\rho_N = \frac{N}{V} = \frac{nN_A}{V} = \frac{pN_A}{RT} = \frac{p}{RT} N_A$$

We have a value for  $p/RT$  from part a of the problem, and so

$$\rho_N = \frac{0.341 \text{ mol}}{\text{m}^3} \frac{6.022 \times 10^{23} \text{ molecule}}{\text{mol}} \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 2.05 \times 10^{17} \text{ molecule}/\text{cm}^3$$

c) There are several ways of doing this problem. One method is to find the average molecular mass of a molecule in the Martian atmosphere, and then convert your answer in a to mass/volume. Since the mol fractions add up to 1, we may say

$$\begin{aligned} M_{\text{ave}} &= X_{\text{CO}_2} M_{\text{CO}_2} + X_{\text{N}_2} M_{\text{N}_2} + X_{\text{Ar}} M_{\text{Ar}} \\ &= (0.955) (44.01 \text{ g/mol}) + (0.026) (28.01 \text{ g/mol}) + (0.019) (39.95 \text{ g/mol}) = 43.52 \text{ g/mol} \end{aligned}$$

$$\text{Since } \frac{n}{V} = \frac{p}{RT}$$

then multiplying both sides of the equation by  $M_{\text{ave}}$  gives

$$\frac{nM_{\text{ave}}}{V} = \frac{m}{V} = \frac{pM_{\text{ave}}}{RT} = \frac{p}{RT} M_{\text{ave}}$$

We have a value for  $p/RT$  from part a of the problem, and so

$$D = \frac{0.341 \text{ mol}}{\text{m}^3} \frac{43.52 \text{ g}}{\text{mol}} = 14.8 \text{ g}/\text{m}^3$$

2) There are several ways of doing this problem. One method is to start by finding the average mass of a chlorine atom in the sample of chlorine. Assuming the ideal gas law applies

$$pV = nRT$$

so  $\frac{n}{V} = \frac{p}{RT}$  If we multiply both sides by  $M_{\text{ave,Cl}_2}$ , the average mass of a  $\text{Cl}_2$  molecule in the sample, then

$$\frac{nM_{\text{ave,Cl}_2}}{V} = \frac{m}{V} = D = \frac{pM_{\text{ave,Cl}_2}}{RT}$$

$$\text{or } M_{\text{ave,Cl}_2} = \frac{DRT}{p} = \frac{(4.168 \times 10^{-3} \text{ g/L}) (0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (273.15 \text{ K})}{(1.0000 \text{ torr}) (1 \text{ atm}/760 \text{ torr})} = 71.00 \text{ g/mol} = 71.00 \text{ amu}$$

Since each Cl<sub>2</sub> molecule contains two Cl atoms, the average mass of a Cl atom is

$$M_{\text{ave,Cl}} = 71.00 \text{ amu}/2 = 35.50 \text{ amu}$$

If we define the mol fraction of <sup>35</sup>Cl as X<sub>35Cl</sub>, then the mol fraction of <sup>37</sup>Cl is (1 - X<sub>35Cl</sub>), and

$$M_{\text{ave,Cl}} = X_{35\text{Cl}} M_{35\text{Cl}} + X_{37\text{Cl}} M_{37\text{Cl}} = X_{35\text{Cl}} M_{35\text{Cl}} (1 - X_{35\text{Cl}}) M_{37\text{Cl}}$$

$$M_{\text{ave,Cl}} = X_{35\text{Cl}} M_{35\text{Cl}} + M_{37\text{Cl}} - X_{35\text{Cl}} M_{37\text{Cl}} = X_{35\text{Cl}} (M_{35\text{Cl}} - M_{37\text{Cl}}) + M_{37\text{Cl}}$$

$$M_{\text{ave,Cl}} - M_{37\text{Cl}} = X_{35\text{Cl}} (M_{35\text{Cl}} - M_{37\text{Cl}})$$

or, solving for X<sub>35Cl</sub>

$$X_{35\text{Cl}} = \frac{M_{\text{ave,Cl}} - M_{37\text{Cl}}}{M_{35\text{Cl}} - M_{37\text{Cl}}} = \frac{(35.50 - 36.965)}{(34.969 - 36.965)} = 0.73$$

So 73% of chlorine atoms (by number) are <sup>35</sup>Cl, and 27% are <sup>37</sup>Cl atoms. This is close to the actual values of 75.8% <sup>35</sup>Cl and 24.2% <sup>37</sup>Cl, found using mass spectrometry.

3) a) The number of moles of CO in the gas cylinder is

$$n = \frac{m}{M} = \frac{158.3 \text{ g}}{28.01 \text{ g/mol}} = 5.652 \text{ mol CO}$$

From the ideal gas law

$$pV = nRT$$

$$\text{So } p = \frac{nRT}{V} = \frac{(5.652 \text{ mol})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(295.2 \text{ K})}{1.640 \text{ L}} = 83.5 \text{ atm}$$

b) From the van der Waals equation

$$(p + an^2/V^2)(V - nb) = nRT$$

$$\begin{aligned} \text{So } p &= \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \\ &= \frac{(5.652 \text{ mol})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(295.2 \text{ K})}{[1.640 \text{ L} - (5.652 \text{ mol})(0.0395 \text{ L/mol})]} - \frac{(1.453 \text{ L}^2\cdot\text{atm/mol}^2)(5.652 \text{ mol})^2}{(1.640 \text{ L})^2} \\ &= 96.64 \text{ atm} - 17.26 \text{ atm} = 79.4 \text{ atm} \end{aligned}$$

Note that this is about 5 percent lower than the value obtained from the ideal gas law.

c) Because the conditions are not quite ideal, I would expect the van der Waals equation to give a better value for pressure than the ideal gas law.

4) a)  $T_c$  represents the highest temperature for which an isothermal reversible compression of a gas will lead to a distinct  $g \rightarrow \ell$  phase transition (a point where a distinct liquid and vapor phase will exist in the system). Above this temperature, the transition from gas to liquid is continuous, and two distinct phases are not observed as the compression takes place.

b) Using the values for the van der Waals  $a$  and  $b$  coefficients from problem 3, we get

$$p_c = \frac{(1.453 \text{ L}^2 \cdot \text{atm/mol}^2)}{27 (0.0395 \text{ L/mol})^2} = 34.5 \text{ atm}$$

$$V_{m,c} = 3b = 3 (0.0395 \text{ L/mol}) = 0.1185 \text{ L} (1000. \text{ cm}^3/\text{L}) = 118.5 \text{ cm}^3$$

$$T_c = \frac{8 (1.453 \text{ L}^2 \cdot \text{atm/mol}^2)}{27 (0.0395 \text{ L/mol}) (0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})} = 132.8 \text{ K}$$

c) The calculated values for  $p_c$  and  $T_c$  are close to the experimental values (likely within the uncertainty in the calculation). The calculated value for  $V_{m,c}$  is about 27% higher than the experimental value. This is due to the fact that the van der Waals correction assumes interactions between molecules occur only for pairs of molecules, while at the critical point all of the molecules are in contact with one another.

5) a)  $\sigma = \pi d^2$ , and so

$$d = (\sigma/\pi)^{1/2} = (0.42 \text{ nm}^2/\pi)^{1/2} = 0.37 \text{ nm}$$

$$b) v_{\text{rms}} = (3RT/M)^{1/2} = [3 (8.314 \text{ J/mol} \cdot \text{K}) (288. \text{ K})/29.0 \times 10^{-3} \text{ kg/mol}]^{1/2} = 498. \text{ m/s}$$

$$c) \lambda = \frac{(1.381 \times 10^{-23} \text{ J/K}) (288. \text{ K})}{2^{1/2} (0.42 \times 10^{-18} \text{ m}^2) (1.00 \text{ atm}) (1.013 \times 10^5 \text{ Pa/atm})} = 6.6 \times 10^{-8} \text{ m} = 66. \text{ nm}$$

$$d) z = \frac{2(0.42 \times 10^{-18} \text{ m}^2)(1.00 \text{ atm})(1.013 \times 10^5 \text{ Pa/atm}) [8(8.314 \text{ J/mol} \cdot \text{K})(288 \text{ K})/\pi(29.0 \times 10^{-3} \text{ kg/mol})]^{1/2}}{(1.381 \times 10^{-23} \text{ J/K}) (288. \text{ K})}$$

$$= 9.8 \times 10^9 \text{ collisions/s}$$

So, in approximate terms, the size of a molecule of air is  $\sim 0.3 \text{ nm}$ . At room temperature and pressure, an air molecule is moving at  $\sim 500 \text{ m/s}$ , travels  $\sim 70 \text{ nm}$  between collisions, and makes  $\sim 10^{10}$  collisions per second.