

CHEMISTRY 311 PHYSICAL CHEMISTRY
Homework Assignment # 1

1. This question makes use of Fig. 1.6 in the text book (p. 9). Assume that the liquid in the manometer has a density of 6.34 g/cm^3 . (a) What is the pressure measured in Fig. 1.6(a) if $h = 340 \text{ mm}$, and $P_{atm} = 760 \text{ torr}$? (b) If $h = 340 \text{ mm}$ in 1.6(b), what is the pressure of the gas? Does the answer depend on P_{atm} ?

Answer

From the formula given in 1.6(a), for the first case, we get $P = P_{atm} \pm \rho gh$, depending on the case treated. For consistency of units, we must either convert P_{atm} to mm of the manometric liquid, or we must convert both terms on the right hand side to standard units. Recall that $1 \text{ bar} = 10^5 \text{ Pa} = 750 \text{ torr}$. Also remember that $\text{Pa} = \text{N m}^{-2} = (\text{kg m s}^{-2}) \text{ m}^{-2}$.

- (a) In the first case, $P = P_{atm} + \rho gh$:

$$\begin{aligned} P &= 760 \text{ torr} \times \left(\frac{10^5 \text{ Pa}}{750 \text{ torr}} \right) + 6.34 \text{ g cm}^{-3} \times \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{10^6 \text{ cm}^3}{1 \text{ m}^3} \right) \times 9.8 \text{ m s}^{-2} \times 0.340 \text{ m} \\ &= 1.2246 \times 10^5 \text{ Pa} = 1.2246 \text{ bar} \\ &= 1.2246 \text{ bar} \times \left(\frac{750 \text{ torr}}{1 \text{ bar}} \right) = 918.45 \text{ torr} \end{aligned}$$

In the second case, $P = P_{atm} - \rho gh$

$$\begin{aligned} P &= 760 \text{ torr} \times \left(\frac{10^5 \text{ Pa}}{750 \text{ torr}} \right) - 6.34 \text{ g cm}^{-3} \times \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{10^6 \text{ cm}^3}{1 \text{ m}^3} \right) \times 9.8 \text{ m s}^{-2} \times 0.340 \text{ m} \\ &= 0.8021 \times 10^5 \text{ Pa} = 0.8021 \text{ bar} \\ &= 0.8021 \text{ bar} \times \left(\frac{750 \text{ torr}}{1 \text{ bar}} \right) = 601.56 \text{ torr} \end{aligned}$$

- (b) In this case, we are using a sealed manometer, which means that $P = \rho gh$. We will convert the calculated pressure to more standard units.

$$\begin{aligned} P &= 6.34 \text{ g cm}^{-3} \times \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{10^6 \text{ cm}^3}{1 \text{ m}^3} \right) \times 9.8 \text{ m s}^{-2} \times 0.340 \text{ m} \\ &= 21124.9 \text{ Pa} = 0.211 \text{ bar} = 158.44 \text{ torr} \end{aligned}$$

In this case, the measured pressure does not depend on the atmospheric pressure.

2. A balloon filled with helium gradually shrinks and loses its buoyancy in air over several hours. Explain why this happens using the principles of the kinetic molecular theory. What qualitative statement can you make about the composition of the gas inside the balloon after several hours, assuming that it was 100% Helium initially.

Answer

The balloon shrinks because it loses helium over time. Atoms of helium are lighter and, therefore, move faster at a given temperature than heavier molecules like N_2 , O_2 , and CO_2 , the predominant constituents of air. Graham's law of diffusion, which is based on kinetic molecular theory, gives the relative rates of diffusion of the two gases as (p. 23 of text)

$$\frac{\text{rate}(\text{He})}{\text{rate}(\text{air})} = \sqrt{\frac{M_{\text{air}}}{M_{\text{He}}}},$$

where it is understood that M_{air} refers to a weighted average of the molecular masses of N_2 , O_2 , and CO_2 , and other trace gases. Also, He atoms are smaller than the molecules in air, and diffuse through the pores of the balloon more readily. The net effect is that the balloon loses helium, and only a part of that loss is replaced by air diffusing in. As a result, the balloon shrinks in size, and loses buoyancy.

3. One mole of a gas at 5.69 bar and 282 K is found to be in a corresponding state with Methane at 4 bar and 300 K. From the table of critical constants given on p. 24 of the textbook, identify the gas.

Answer

Since the two gases are in corresponding states, their reduced pressures and temperatures are equal. For methane, $T_C = 190.6$ K, $P_C = 46.4$ bar. Therefore,

$$T_R = \frac{300}{190.6} = 1.574; \quad P_R = \frac{4.0}{46.4} = 0.0862$$

For the unknown gas,

$$T_C = \frac{T}{T_R} = \frac{282 \text{ K}}{1.574} = 182.9 \text{ K}$$

$$P_C = \frac{P}{P_R} = \frac{5.69 \text{ bar}}{0.0862} = 66.0 \text{ bar}$$

From the table of critical constants, the unknown gas is identified to be NO.

4. (a) The Virial coefficient $B(T)$ of carbon dioxide is $-149.7 \text{ cm}^3 \text{ mol}^{-1}$ at 0°C . Compare its compressibility factor Z at this temperature and 1 bar with that of an ideal gas. [Hint: Substitute for V in terms of the ideal gas law on the right hand side of Eq. (1.117) to get an equation similar to Eq. (1.116); ignore terms containing P^2 and higher powers of P .] (b) Calculate the second Virial coefficient of Methane at 300 K from its van der Waals constants (see Table 1.5), using the relationship obtained from Problem 1.55 of the textbook, and calculate the compressibility factor at 300 K and 1 bar.

Answer

- (a) From Eq. (1.118), substituting $V = nRT/P$, we get an approximate expression in terms of pressure:

$$Z = 1 + B(T) \frac{n}{V} + \dots$$

$$\simeq 1 + \left(\frac{B}{RT} \right) P + \dots$$

$$= 1 + \left(\frac{-149.7 \text{ cm}^3 \text{ mol}^{-1} \times 1.0 \text{ L}/1000 \text{ cm}^3}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}} \right) \times 1 \text{ bar}$$

$$= 0.9934$$

The compressibility factor for an ideal gas would be identically equal to 1.

- (b) The van der Waals constants for methane: $a = 0.2283 \text{ Pa m}^6 \text{ mol}^{-2} = 2.283 \text{ bar L}^2 \text{ mol}^{-2}$, and $b = 0.0428 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} = 0.0428 \text{ L mol}^{-1}$. From the solution to the assigned problem (1.55) in the text,

$$B(T) = \left(b - \frac{a}{RT} \right) = -0.0487 \text{ L mol}^{-1}.$$

$$C(T) = b^2 \text{ L}^2 \text{ mol}^{-2} = 1.83 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2}$$

Compressibility factor is

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

Substituting for $V_m = RT/P$, we get

$$\begin{aligned} Z &= 1 + \left(b - \frac{a}{RT}\right) \frac{P}{RT} + \frac{b^2}{(RT)^2} P^2 + \dots \\ &= 1 - 0.0487 \text{ L mol}^{-1} \times \frac{1 \text{ bar}}{0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \\ &\quad + \frac{1.83 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2}}{(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K})^2} \\ &= 0.9981 \end{aligned}$$