

## Chem 338

### Homework Set #1 solutions

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From Atkins: 0.2, 1.5, 1.6, 1.10, 1.13, 1.21, 1.25, 1.29

- 0.2)** Calculate the pressure in the Mindañao trench, near the Philippines, the deepest region of the oceans. Take the depth there as 11.5 km and for the density of sea water use  $1.10 \text{ g cm}^{-3}$ .

Since pressure is defined as force per unit area, this becomes the following:

$P = \rho gh$ , where  $g$  = acceleration of free fall =  $9.81 \text{ m/s}^2$ ,  $\rho$  is the density of sea water, and  $h$  is the depth.

First some unit conversions and plug-in:

$$\rho = 1.10 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 1.10 \times 10^3 \frac{\text{kg}}{\text{m}^3}$$

$$h = 11.5 \text{ km} \times \frac{1000 \text{ m}}{\text{km}} = 1.15 \times 10^4 \text{ m}$$

$$P = \left( 9.81 \frac{\text{m}}{\text{s}^2} \right) \times \left( 1.10 \times 10^3 \frac{\text{kg}}{\text{m}^3} \right) \times \left( 1.15 \times 10^4 \text{ m} \right) = 1.24 \times 10^8 \text{ Pa}$$

- 1.5)** The effect of high pressure on organisms, including humans, is studied to gain information about deep-sea diving and anaesthesia. A sample of air occupies 1.00 L at  $25^\circ\text{C}$  and 1.00 atm. What pressure is needed to compress it to  $100 \text{ cm}^3$  at this temperature?

Since both the temperature and amount of air remains the same in both states, we can use the relation:

$$P_1 V_1 = P_2 V_2 \quad \text{at } T_1, n$$

$$P_2 = \frac{P_1 V_1}{V_2}$$

$100 \text{ cm}^3 = 0.100 \text{ L}$ , so:

$$P_2 = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{0.100 \text{ L}} = 10.0 \text{ atm}$$

- 1.6)** You are warned not to dispose of pressurized cans by throwing them on to a fire. The gas in an aerosol container exerts a pressure of 125 kPa at 18°C. The container is thrown on a fire, and its temperature rises to 700°C. What is the pressure at this temperature?

In this case, since the volume and amount of gas is the same in both states, we can use the relation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ ,or: } P_2 = P_1 \frac{T_2}{T_1}$$

converting to kelvin  $T_1 = 291.15 \text{ K}$ ,  $T_2 = 973.15 \text{ K}$  and plugging in:

$$P_2 = (125 \text{ kPa}) \frac{973.15 \text{ K}}{291.15 \text{ K}} = 418 \text{ kPa}$$

- 1.10)** At sea level, where the pressure was 104 kPa and the temperature 21.1°C, a certain mass of air occupied 2.0 m<sup>3</sup>. To what volume will the region expand when it has risen to an altitude where the pressure and temperature are (a) 52 kPa, -5.0°C, (b) 880 Pa, -52.0°C?

We can either first calculate how many moles of air we have given the initial conditions or use the relation  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  (for fixed  $n$ ). Using the latter:

$$(a) V_2 = \frac{P_1 T_2}{P_2 T_1} V_1 = \frac{(104 \text{ kPa})(268.15 \text{ K})}{(52 \text{ kPa})(294.25 \text{ K})} (2.0 \text{ m}^3) = 3.6 \text{ m}^3$$

$$(b) V_2 = \frac{(104 \text{ kPa})(221.15 \text{ K})}{(0.880 \text{ kPa})(294.25 \text{ K})} (2.0 \text{ m}^3) = 177.6 \text{ m}^3$$

**1.13)** A gas mixture being used to simulate the atmosphere of another planet consists of 320 mg of methane, 175 mg of argon, and 225 mg of nitrogen. The partial pressure of nitrogen at 300 K is 15.2 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

First we need to convert masses to moles:

$$0.320 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.042 \text{ g}} = 1.9948 \times 10^{-2} \text{ mol}$$

$$0.175 \text{ g Ar} \times \frac{1 \text{ mol Ar}}{39.95 \text{ g}} = 4.3805 \times 10^{-3} \text{ mol}$$

$$0.225 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g}} = 8.0300 \times 10^{-3} \text{ mol}$$

(a)

$$V = \frac{nRT}{P} = \frac{n_{\text{N}_2} RT}{P_{\text{N}_2}} = \frac{(8.0300 \times 10^{-3} \text{ mol})(8.31451)(300 \text{ K})}{15.2 \times 10^3 \text{ Pa}} = 0.00132 \text{ m}^3 = 1.32 \text{ L}$$

$$(b) P = \frac{RT}{V} \sum_i n_i = \frac{(8.31451)(300 \text{ K})}{1.32 \text{ L}} (0.03236 \text{ mol}) = 61.1 \text{ kPa}$$

OR in terms of the mole fraction of N<sub>2</sub>:

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{total}}} = \frac{0.008030}{0.032358} = 0.24816$$

$$P_{\text{total}} = \frac{P_{\text{N}_2}}{x_{\text{N}_2}} = \frac{15.2}{0.24816} = 61.2 \text{ kPa}$$

**1.21)** When we are studying the photochemical processes that can occur in the upper atmosphere, we need to know how often atoms and molecules collide. At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of N<sub>2</sub> molecules? Take  $\sigma = 0.43 \text{ nm}^2$ .

$$P = 0.050 \text{ atm} \times \frac{101.325 \text{ kPa}}{\text{atm}} = 5.066 \text{ kPa}$$

$$\sigma = 0.43 \text{ nm}^2 = 0.43 \times 10^{-18} \text{ m}^2$$

$$\lambda = \frac{RT}{\sqrt{2}N_A\sigma P} = \frac{(8.31451)(217\text{ K})}{(\sqrt{2})(6.02214 \times 10^{23})(0.43 \times 10^{-18}\text{ m})(5.066 \times 10^3\text{ Pa})}$$

$$= 9.7 \times 10^{-7}\text{ m} = 0.97\ \mu\text{m}$$

Note that this is 970 nm, which is about 2600 molecular diameters.

**1.25)** The spread of pollutants through the atmosphere is governed partly by the effects of winds but also by the natural tendency of molecules to diffuse. The latter depends on how far a molecule can travel before colliding with another molecule. Calculate the mean free path of diatomic molecules in air using  $\sigma=0.43\text{ nm}^2$  at 25°C and (a) 10 bar, (b) 103 kPa, (c) 1Pa.

Following the same procedure as 1.21 above,

$$(a) P = 10\text{ bar} = 1 \times 10^6\text{ Pa}, \quad \lambda = 0.68 \times 10^{-8}\text{ m} = 6.8\text{ nm}$$

$$(b) P = 103\text{ kPa} = 103 \times 10^3\text{ Pa}, \quad \lambda = 0.66 \times 10^{-7}\text{ m} = 66\text{ nm}$$

$$(c) P = 1\text{ Pa}, \quad \lambda = 0.68 \times 10^{-2}\text{ m} = 7\text{ mm}$$

**1.29)** How reliable is the perfect gas law in comparison with the van der Waals equation? Calculate the difference in pressure of 10.00 g of carbon dioxide confined to a container of volume 100 cm<sup>3</sup> at 25.0°C between treating it as a perfect gas and a van der Waals gas.

Let's do some unit conversions first:

$$100\text{ cm}^3 \times \left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 = 1 \times 10^{-4}\text{ m}^3$$

$$10.00\text{ g CO}_2 \times \frac{1\text{ mol}}{44.01\text{ g}} = 0.22722\text{ mol CO}_2$$

$$25.0^\circ\text{C} = 298.15\text{ K}$$

for a perfect gas:

$$P = \frac{nRT}{V} = \frac{(0.22722\text{ mol})(8.31451)(298.15\text{ K})}{1 \times 10^{-4}} = 5.633 \times 10^6\text{ Pa}$$

for a van der Waals gas:

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

for CO<sub>2</sub>,  $a = 3.59 \frac{\text{L}^2 \text{atm}}{\text{mol}^2}$  and  $b = 0.043 \frac{\text{L}}{\text{mol}}$

$$3.59 \frac{\text{L}^2 \text{atm}}{\text{mol}} \times \left(\frac{10^{-3} \text{m}^3}{\text{L}}\right)^2 \times \frac{101323 \text{ Pa}}{\text{atm}} = 0.3637 \frac{\text{m}^6 \text{Pa}}{\text{mol}}$$

$$0.043 \frac{\text{L}}{\text{mol}} \times \frac{10^3 \text{ cm}^3}{\text{L}} \times \frac{10^{-6} \text{ m}^3}{\text{cm}^3} = 4.30 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

plugging everything into the vdW eqn.:

$$P = \frac{(0.22722)(8.31451)(298.15 \text{ K})}{1 \times 10^{-4} - (0.22722)(4.3 \times 10^{-5})} - (0.3637) \left(\frac{0.22722}{1 \times 10^{-4}}\right)^2$$
$$= 4.365 \times 10^6 \text{ Pa}$$

$$\Delta P = P_{\text{perfect}} - P_{\text{vdW}} = 1.27 \text{ MPa (29\%)}$$

So a pretty big difference, but these are fairly high pressures too where we might expect the perfect gas equation of state to be not very accurate.