

Homework 1 Solutions

1. The external (atmospheric) pressure is greater than the internal pressure, hence

$$\rho_{\text{ex}} - \rho_{\text{in}} = \rho gh$$

$$\rho_{\text{in}} = \rho_{\text{ex}} - \rho gh = 758 \text{ Torr} - \rho gh$$

ρgh can be expressed in Torr as follows

$$\rho gh = 3.55 \text{ cm H}_2\text{O} \times (1 \text{ cm Hg} / 13.59 \text{ cm H}_2\text{O}) = 0.261 \text{ cm Hg} = 2.61 \text{ mm Hg} \\ = 2.61 \text{ Torr}$$

$$\rho_{\text{in}} = 758 \text{ Torr} - 2.61 \text{ Torr} = \mathbf{755.39 \text{ Torr}}$$

2. At $T = 0$, $\theta_{\text{Celsius}}/^{\circ}\text{C} = -273.15$

We solve the equation for $\theta_{\text{Fahrenheit}}/^{\circ}\text{F} = t_{\text{F}}$

$$-273.15 = 5/9 (t_{\text{F}} - 32)$$

$$t_{\text{F}} = -273.15 \times (9/5) + 32 = -459.67$$

$$\theta_{\text{Fahrenheit}} (\text{at } T = 0) = \mathbf{-459.67^{\circ}\text{F}}$$

3. Boyle's law can be applied: $p_i V_i = p_f V_f$

$$\text{Therefore, } p_i = p_f V_f / V_i = (5.04 \text{ bar}) \times (4.65 \text{ dm}^3) / (4.65 + 2.20) \text{ dm}^3 = \mathbf{3.42 \text{ bar}}$$

For (b), we convert bar to atm: 1 atm = 1.013 bar

$$p_i = (3.42 \text{ bar}) \times (1 \text{ atm}) / (1.013 \text{ bar}) = \mathbf{3.38 \text{ atm}}$$

4.

The relation between pressure and temperature at constant volume can be derived from the perfect gas law

$$pV = nRT \quad \text{so} \quad p \propto T \quad \text{and} \quad \frac{p_i}{T_i} = \frac{p_f}{T_f}$$

The final pressure, then, ought to be

$$p_f = p_i T_f / T_i$$

Internal pressure = pump pressure + atmospheric pressure.

$$p_i = (24 + 14.7) \text{ lb in}^{-2} = 38.7 \text{ lb in}^{-2}$$

$$T_i = -5 + 273 = 268 \text{ K} \quad T_f = 35 + 273 = 308 \text{ K}$$

$$p_f = (38.7 \text{ lb in}^{-2}) \times (308 \text{ K}) / (268 \text{ K}) = 44.5 \text{ lb in}^{-2}$$

$$\text{Therefore, } p(\text{pump}) = (44.5 - 14.7) \text{ lb in}^{-2} = \mathbf{29.8 \text{ lb in}^{-2}}$$

5. We use the perfect gas equation of state: $pV = nRT$

Therefore, $R = pV/nT$

First, calculate pressure:

$$p = \rho gh = \{0.99707 \times 10^{-3} \text{ kg} / (10^{-6} \text{ m}^3)\} \times (9.8067 \text{ m s}^{-2}) \times (206.402 \times 10^{-2} \text{ m}) \\ = 2.0182 \times 10^4 \text{ Pa}$$

$$V = 20.000 \text{ dm}^3 = 2.0000 \times 10^{-2} \text{ m}^3$$

$$n = m/M = (0.25132 \text{ g}) / (4.00260 \text{ g mol}^{-1}) = 0.062789 \text{ mol}$$

$$R = (2.0182 \times 10^4 \text{ Pa}) \times (2.0000 \times 10^{-2} \text{ m}^3) / \{(0.062789 \text{ mol}) \times (773.15 \text{ K})\} \\ = \mathbf{8.3147 \text{ J K}^{-1} \text{ mol}^{-1}}$$

6. To calculate the molar mass of the compound, we need to relate density, temperature, and pressure. Using the perfect gas law:

$$pV = nRT \quad \text{and} \quad \text{density} = \text{mass} / \text{volume}$$

$$V = nRT/p \quad \text{and} \quad m/\rho = nRT/p$$

To calculate molar mass, use $n = 1$. Then, $M = \rho RT/p$

$$M = (1.23 \text{ g L}^{-1})(8.3145 \text{ kPa L K}^{-1} \text{ mol}^{-1})(330 \text{ K}) / (20.0 \text{ kPa}) = \mathbf{169 \text{ g mol}^{-1}}$$

7. (a) For a perfect gas $p = nRT/V$ for (i) $n = 1.0 \text{ mol}$, $R = 8.2058 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$, $T = 273.15$ in 22.414 L .

$$p = (1.0 \text{ mol}) \times (8.2058 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K}) / (22.414 \text{ L}) = \mathbf{1.0 \text{ atm}}$$

For (ii) $T = 1000 \text{ K}$ and $V = 100 \text{ cm}^3$

$$p = (1.0 \text{ mol}) \times (8.2058 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (1000 \text{ K}) / (0.1 \text{ L}) = \mathbf{8.2 \times 10^2 \text{ atm}}$$

(b) For a van der Waals gas, using Table 1.6, $a = 5.507 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.0651 \text{ L mol}^{-1}$, the van der Waals equation is

$$p = nRT/(V-nb) - a(n/V)^2$$

$$(i) \quad p = (1.0 \text{ mol}) \times (8.2058 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K}) / (22.414 \text{ L} - (1.0 \text{ mol}) \times (0.0651 \text{ L mol}^{-1})) - 5.507 \text{ L}^2 \text{ atm mol}^{-2} \times (1.0 \text{ mol} / 22.414 \text{ L})^2 = \mathbf{1.0 \text{ atm}}$$

$$(ii) \quad p = (1.0 \text{ mol}) \times (8.2058 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (1000 \text{ K}) / (0.1 \text{ L} - (1.0 \text{ mol}) \times (0.0651 \text{ L mol}^{-1})) - 5.507 \text{ L}^2 \text{ atm mol}^{-2} \times (1.0 \text{ mol} / 0.1 \text{ L})^2 = \mathbf{1.7 \times 10^3 \text{ atm}}$$

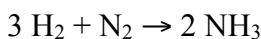
8. van der Waals equation:
$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Solving for b , we obtain
$$b = V_m - \frac{RT}{\left(p + \frac{a}{V_m^2}\right)}$$

$$b = 5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) / \{(3.0 \times 10^6 \text{ Pa}) + (0.50 \text{ m}^6 \text{ Pa mol}^{-2}) / (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2\} = \mathbf{0.46 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}$$

$$Z = pV_m/RT = (3.0 \times 10^6 \text{ Pa}) \times (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}) / \{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})\} = \mathbf{0.66}$$

9. The chemical reaction that will occur is



3.0 mol H_2 are needed to react with 1.0 mol N_2 , but only 2.0 mol H_2 are available, so only $2/3$ mol N_2 will react with these 2.0 mol H_2 to produce $4/3$ mol NH_3 . After the reaction is completed the mixture in the vessel will contain $1 - 2/3 = 1/3$ mol N_2 and $4/3$ mol NH_3 .

Then,

$$p(\text{N}_2) = n(\text{N}_2)RT/V = (1/3) \times 8.20574 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273.15 \text{ K} / 22.4 \text{ L} = \mathbf{0.33 \text{ atm}}$$

$$p(\text{NH}_3) = n(\text{NH}_3)RT/V = (4/3) \times 8.20574 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273.15 \text{ K} / 22.4 \text{ L} = \mathbf{1.33 \text{ atm}}$$

$$p = p(\text{N}_2) + p(\text{NH}_3) = \mathbf{1.66 \text{ atm}}$$

10. By definition, $Z = V_m/V_m^0$, where V_m^0 is the molar volume of a perfect gas.

$$p(V - nb) = nRT \quad p(V_m - b) = RT$$

Therefore,

$$V_m = RT/p + b$$

On the other hand, from the perfect gas equation,

$$pV_m^0 = RT \quad \text{and} \quad V_m^0 = RT/p$$

$$\text{So,} \quad V_m = V_m^0 + b \quad \text{and} \quad Z = V_m/V_m^0 = (V_m^0 + b)/V_m^0 = \mathbf{1 + b/V_m^0}$$

$$\text{If} \quad V_m = 10b \quad V_m^0 = 9b \quad \text{and} \quad \mathbf{Z = 10/9}$$