Physical Chemistry I (Chem 331) – Fall 2009
Solutions to Problem Set 1

1) A perfect gas undergoes isothermal compression, which reduces its volume by 3.08 dm³. The final pressure and volume of the gas are 6.42 bar and 5.38 dm³, respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.

Boyle's law [1.6] in the form $p_f V_f = p_i V_i$ can be solved for either initial or final pressure, hence

$$p_i = \frac{V_f}{V_i} \times p_f$$

$V_f = 5.38\,\text{dm}^3, \qquad V_i = 5.38\,\text{dm}^3 + 3.08\,\text{dm}^3 = 8.46\,\text{dm}^3, \qquad p_f = 6.42\,\text{bar}$

Therefore,

(a) $\qquad p_i = \left(\frac{5.38\,\text{dm}^3}{8.46\,\text{dm}^3}\right) \times (6.42\,\text{bar}) = \boxed{4.08\,\text{bar}}$

(b) Since 1 atm = 1.013 bar, $p_i = (4.08\,\text{bar}) \times \left(\frac{1\,\text{atm}}{1.013\,\text{bar}}\right) = \boxed{4.03\,\text{atm}}$

2) At 0.000° C and 1.000 atm, the mass density of the vapor of a hydrocarbon is 1.97 kg m⁻³. What is the molecular formula of the hydrocarbon under these conditions? What is the hydrocarbon?

Since $p < 1\,\text{atm}$, the approximation that the vapour is a perfect gas is adequate. Then (as in Exercise 1.7(b)),

$$pV = nRT = \frac{m}{M}RT. \text{ Upon rearrangement,}$$

$$M = \rho\left(\frac{RT}{p}\right) = (1.97\,\text{kg m}^{-3}) \times \frac{(8.314\,\text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}{1.013 \times 10^5\,\text{Pa}} = 0.0441\,\text{kg mol}^{-1} = \boxed{44.1\,\text{g mol}^{-1}}$$

The formula of the vapour is then $\boxed{C_3H_8}$, which is one of the propanes.

3) Calculate the pressure exerted by 1.0 mol C_6H_6 behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 373.15 K in 22.414 dm³, (ii) at 1000 K in 300 cm³.

$$p = \frac{nRT}{V} \; [1.8]$$

$$n = 1.0 \, \text{mol}, \qquad T = 373.15 \, \text{K (i)} \quad \text{or} \quad 1000 \, \text{K (ii)}$$

$$V = 22.414 \, \text{dm}^3 \; \text{(i)} \quad \text{or} \quad 300 \, \text{cm}^3 \; \text{(ii)}$$

(i) $\quad p = \dfrac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2} \, \text{dm}^3 \, \text{atm} \, \text{K}^{-1} \text{mol}^{-1}) \times (373.15 \, \text{K})}{22.414 \, \text{dm}^3} = \boxed{1.37 \, \text{atm}}$

(ii) $\quad p = \dfrac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2} \, \text{dm}^3 \, \text{atm} \, \text{K}^{-1} \text{mol}^{-1}) \times (1000 \, \text{K})}{0.300 \, \text{dm}^3} = \boxed{2.73 \times 10^2 \, \text{atm}}$

(b) $\quad p = \dfrac{nRT}{V-nb} - \dfrac{an^2}{V^2} \, [1.21a]$

From Table 1.5, $a = 5.507 \, \text{dm}^6 \, \text{atm} \, \text{mol}^{-2}$ and $b = 6.51 \times 10^{-2} \, \text{dm}^3 \, \text{mol}^{-1}$. Therefore,

(i) $\quad \dfrac{nRT}{V-nb} = \dfrac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2} \, \text{dm}^3 \, \text{atm} \, \text{K}^{-1} \text{mol}^{-1}) \times (373.15 \, \text{K})}{[22.414 - (1.0) \times (6.51 \times 10^{-2})] \, \text{dm}^3} = 1.37 \, \text{atm}$

$\dfrac{an^2}{V^2} = \dfrac{(5.507 \, \text{dm}^6 \, \text{atm} \, \text{mol}^{-2}) \times (1.0 \, \text{mol})^2}{(22.414 \, \text{dm}^3)^2} = 1.1\bar{1} \times 10^{-2} \, \text{atm}$

and $p = 1.37 \, \text{atm} - 1.1\bar{1} \times 10^{-2} \, \text{atm} = \boxed{1.36 \, \text{atm}}$

(ii) $\quad \dfrac{nRT}{V-nb} = \dfrac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2} \, \text{dm}^3 \, \text{atm} \, \text{K}^{-1} \text{mol}^{-1}) \times (1000 \, \text{K})}{(0.300 - 0.0651) \, \text{dm}^3}$

$= 3.4\bar{9} \times 10^2 \, \text{atm}$

$\dfrac{an^2}{V^2} = \dfrac{(5.507 \, \text{dm}^6 \, \text{atm} \, \text{mol}^{-2}) \times (1.0 \, \text{mol})^2}{(0.300 \, \text{dm}^3)^2} = 1.8\bar{3} \times 10^2 \, \text{atm}$

and $p = 3.4\bar{9} \times 10^2 \, \text{atm} - 1.8\bar{4} \times 10^2 \, \text{atm} = \boxed{1.65 \times 10^2 \, \text{atm}}$

4) A certain gas obeys the van der Waals equation with a = 0.580 m⁶ Pa mol⁻². Its volume is found to be 3.50 × 10–4 m³ mol⁻¹ at 273 K and 5.0 MPa. From this information calculate the van der Waals constant b. What is the compression factor for this gas at the prevailing temperature and pressure?

The van der Waals equation [1.21b] is solved for b, which yields

$$b = V_m - \frac{RT}{\left(p + \dfrac{a}{V_m^2} \right)}$$

Substituting the data

$$b = 3.50 \times 10^{-4}\, \text{m}^3\, \text{mol}^{-1} - \frac{(8.314\,\text{J K}^{-1}\text{mol}^{-1}) \times (273\,\text{K})}{\left\{ (5.0 \times 10^6\, \text{Pa}) + \left(\dfrac{0.580\,\text{m}^6\, \text{Pa mol}^{-2}}{(3.50 \times 10^{-4}\, \text{m}^3\, \text{mol}^{-1})^2} \right) \right\}}$$

$$= \boxed{1.17 \times 10^{-4}\, \text{m}^3\, \text{mol}^{-1}}$$

$$Z = \frac{pV_m}{RT}[1.17] = \frac{(5.0 \times 10^6\, \text{Pa}) \times (3.50 \times 10^{-4}\, \text{m}^3\text{mol}^{-1})}{(8.314\,\text{J K}^{-1}\text{mol}^{-1}) \times (273\,\text{K})} = \boxed{0.77}$$

5) In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 m³. The gas enters the container at 300 K and 100 atm. The mass of the gas is 92.4 kg. Use the van der Waals equation to determine the approximate pressure of the gas at its working temperature of 500 K. For nitrogen, a = 1.352 dm⁶ atm mol⁻², b = 0.0387 dm³ mol⁻¹.

The amount of gas is first determined from its mass; then the van der Waals equation is used to determine its pressure at the working temperature. The initial conditions of 300 K and 100 atm are in a sense superfluous information.

$$n = \frac{92.4\,\text{kg}}{28.02 \times 10^{-3}\,\text{kg mol}^{-1}} = 3.30 \times 10^{3}\,\text{mol}$$

$$V = 1.000\,\text{m}^3 = 1.000 \times 10^3\,\text{dm}^3$$

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}[1.21a] = \frac{(3.30 \times 10^3\,\text{mol}) \times (0.08206\,\text{dm}^3\text{atm K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{(1.000 \times 10^3\,\text{dm}^3) - (3.30 \times 10^3\,\text{mol}) \times (0.0387\,\text{dm}^3\,\text{mol}^{-1})}$$

$$- \frac{(1.352\,\text{dm}^6\,\text{atm mol}^{-2}) \times (3.30 \times 10^3\,\text{mol})^2}{(1.000 \times 10^3\,\text{dm}^3)^2}$$

$$= (155 - 14.8)\,\text{atm} = \boxed{140\,\text{atm}}.$$

6) Suppose that 10.0 mol C_2H_6(g) is confined to 4.860 dm³ at 300 K. Predict the pressure exerted by ethane from a) the ideal gas and b) the van der Waals equations of state. Calculate the compression factor based on these calculations. For ethane, a = 5.507 dm⁶ atm mol⁻², b = 0.0651 dm³ mol⁻¹

(a) $p = \dfrac{nRT}{V}$ [1.8] $= \dfrac{(10.0\,\text{mol}) \times (0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}{4.860\,\text{dm}^3} = \boxed{50.7\,\text{atm}}$.

(b) $p = \dfrac{nRT}{V-nb} - a\left(\dfrac{n}{V}\right)^2$ [1.21a]

$= \dfrac{(10.0\,\text{mol}) \times (0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}{(4.860\,\text{dm}^3) - (10.0\,\text{mol}) \times (0.0651\,\text{dm}^3\,\text{mol}^{-1})}$

$- (5.507\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}) \times \left(\dfrac{10.0\,\text{mol}}{4.860\,\text{dm}^3}\right)^2$

$= 58.4\overline{9} - 23.3\overline{2} = \boxed{35.2\,\text{atm}}$.

The compression factor is calculated from its definition [1.17] after inserting $V_m = \dfrac{V}{n}$.

To complete the calculation of Z, a value for the pressure, p, is required. The implication in the definition [1.17] is that p is the actual pressure as determined experimentally. This pressure is neither the perfect gas pressure nor the van der Waals pressure. However, on the assumption that the van der Waals equation provides a value for the pressure close to the experimental value, we can calculate the compression factor as follows

$Z = \dfrac{pV}{nRT} = \dfrac{(35.2\,\text{atm}) \times (4.860\,\text{dm}^3)}{(10.0\,\text{mol}) \times (0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})} = \boxed{0.695}$.