## Thermodynamics: Examples for chapter 1.

1. When 0.12 g of solid iodine was vaporized at 1670 K, the resulting gas displaced 20.2 cm<sup>3</sup> of dry air at 298 K and 99.9 kPa pressure. How many iodine molecules were dissociated (i.e. as atomic iodine) in the gas? The gas phase equilibrium reaction is:

$$I_2(g) \rightleftharpoons 2I(g)$$

Assume that the gas mixture (of  $I_2$  and I) behave according to the ideal gas law.

Solution:

The amount of  $I_2$  before any dissociation takes place is:

$$n = \frac{m}{M_{\rm I_2}} = \frac{0.12 \text{ g}}{254 \text{ g mol}^{-1}} = 4.7 \times 10^{-4} \text{ mol}$$

After the equilibrium has been reached, the amount of  $I_2$  is  $(1 - \alpha)n$ and the amount of I is  $2\alpha n$ . Here the degree of dissociation is denoted by  $\alpha$ . The ideal gas law is:

$$PV = n_{tot}RT \Rightarrow n_{tot} = \frac{PV}{RT} \Rightarrow n_{tot} = (1 - \alpha)n + 2\alpha n = \frac{PV}{RT}$$
$$\Rightarrow \alpha = \frac{PV}{nRT} - 1$$

$$= \frac{PVM_{I_2}}{mRT} - 1 = \frac{(99.9 \text{ kN m}^{-2}) \times (20.2 \times 10^{-6} \text{m}^3) \times (254 \text{ g mol}^{-1})}{(0.12 \text{ g}) \times (8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} - 1 = 0.72$$

The amount of I is  $2\alpha n = 2 \times 0.72 \times (4.7 \times 10^{-4} \text{ mol}) = 6.8 \times 10^{-4} \text{ mol}.$ 

2. What is the molar volume of *n*-hexane at 660 K and 91 bar according to (a) the ideal gas law and (b) the van der Waals equation? For *n*-hexane,  $T_c = 507.7$  K and  $P_c = 30.3$  bar. If you obtain an equation that you cannot solve analytically, attempt to solve it numerically. Solution:

a)

$$\bar{V} = \frac{RT}{P} = \frac{(0.08314 \text{ L bar } \text{K}^{-1} \text{mol}^{-1})(660 \text{ K})}{91 \text{ bar}} = 0.603 \text{L mol}^{-1}$$

b)

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})^2(507.7 \text{ K})^2}{64(30.3 \text{ bar})} = 24.81 \text{ L}^2 \text{ bar mol}^{-2}$$
$$b = \frac{RT_c}{8P_c} = \frac{(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})(507.7 \text{ K})}{30.3 \text{ bar}} = 0.174 \text{ L mol}^{-1}$$
$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Test values for  $\bar{V}$  and see when you get 91 bars:  $\bar{V} = 0.39 \text{ L mol}^{-1}$ . This equation can also be solved by Maxima:

a : 24.81; b : 0.174; R : 0.08314; T : 660; P : 91; r : solve(P = R\*T/(V - b) - a/(V\*V), V); float(r);

This shows three roots of which only one is real (two are complex). The last line converts the complicated algebraic form to numerical values.

3. Ten grams of  $N_2$  is mixed with 5 g of  $O_2$  and held at 25 °C and 0.750 bar. (a) What are the partial pressures of  $N_2$  and  $O_2$ ? (b) What is the volume of the ideal mixture?

 $\underline{Solution}$ :

a)  

$$n_{N_2} = \frac{10 \text{ g}}{28.013 \text{ g mol}^{-1}} = 0.357 \text{ mol}$$

$$n_{O_2} = \frac{5 \text{ g}}{32.000 \text{ g mol}^{-1}} = 0.156 \text{ mol}$$

$$y_{N_2} = \frac{0.357 \text{ mol}}{0.513 \text{ mol}} = 0.696 \text{ mol}$$

$$y_{O_2} = \frac{0.156 \text{ mol}}{0.513 \text{ mol}} = 0.304 \text{ mol}$$

$$P_{N_2} = 0.696 \times (0.750 \text{ bar}) = 0.522 \text{ bar}$$

$$P_{O_2} = 0.304 \times (0.750 \text{ bar}) = 0.228 \text{ bar}$$
b)

$$V = \frac{nRT}{P} = \frac{(0.513 \text{ mol})(0.083145 \text{ L bar } \text{K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.750 \text{ bar}} = 17.00 \text{ L}$$

4. Calculate dZ/dP for a real gas in the limit  $P \rightarrow 0$  using the virial equation. Solution:

$$Z = 1 + B'P + C'P^2 + \dots \Rightarrow \frac{dZ}{dP} = B' + 2C'P + \dots \Rightarrow \left(\frac{dZ}{dP}\right)_{P \to 0} = B'$$

5. The critical temperature of gaseous ammonia is 406 K and the critical pressure is 113 bar. Use the van der Waals equation to predict its molar volume at 273 K and 1 bar. Hint: Calculate first the coefficients *a* and *b*, then write the equation for the molar volume:  $\bar{V} = \frac{RT}{P+a/\bar{V}^2} + b$ . Guess an initial value for the molar volume and obtain a new value from the equation. Place the obtained value in the equation again to get a new value. Repeat this procedure until the value does not change anymore. This is an example of iterative methods for solving equations.

## Solution:

Use the following equations derived in the lecture notes:

$$a = \frac{27R^2T_c^2}{64P_c}$$
 and  $b = \frac{RT_c}{8P_c}$ 

This gives  $a = 425 \text{ L}^2 \text{ kPa mol}^{-2}$  and  $b = 0.0373 \text{ L mol}^{-1}$ . Use the above equation and iterate until you get convergence:  $\bar{V} = 22.55 \text{ L} \text{ mol}^{-1}$ .

6. Derive the expressions for  $V_c$ ,  $T_c$  and  $P_c$  in terms of the van der Waals constants a and b.

Solution:

The equations in the lecture notes can be rewritten as (the definition of critical point and the equation of state):

$$\frac{RT_c}{\left(\bar{V}_c - b\right)^2} = \frac{2a}{\bar{V}_c^3}$$
$$\frac{2RT_c}{\left(\bar{V}_c - b\right)^3} = \frac{6a}{\bar{V}_c^4}$$
$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}$$

Division of the first equation by the second (side by side) yields  $\bar{V}_c = 3b$ . Substitution of this expression into the first equation above gives  $T_c =$   $\frac{8a}{27Rb}$ . Substitution of the two previous equations into the last equation above yields  $P_c = \frac{a}{27b^2}$ . Note that the van der Waals constants a and b are usually calculated using the critical temperature and pressure since they are typically known more accurately than the critical volume.

7. The isothermal compressibility  $\kappa$  of a gas is defined as:

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Calculate  $\kappa$  for a van der Waals gas using the method of implicit differentiation (with respect to P). Show that in the limit of infinite volume, it yields 1/P (the same result as the ideal gas law).

Solution:

Based on the lecture notes, the van der Waals equation can be written:

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$$

Expand the left hand side and substitute  $\overline{V} = V/n$  to get:

$$nRT = PV - nPb + \frac{n^2a}{V} - \frac{n^3ab}{V^2}$$

Implicit differentiation with respect to P at constant T gives (i.e., side by side):

$$0 = V + P\left(\frac{\partial V}{\partial P}\right)_T - nb - \frac{n^2 a}{V^2} \times \left(\frac{\partial V}{\partial P}\right)_T + \frac{2n^3 ab}{V^3} \times \left(\frac{\partial V}{\partial P}\right)_T$$

Solving for  $\left(\frac{\partial V}{\partial P}\right)_T$  gives:

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{nb - V}{P - n^2 a/V^2 + 2n^3 ab/V^3}$$

The definition of isothermal compressibility now gives (at last stage V is assumed to be large):

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{V - nb}{PV - n^2 a/V + 2n^3 ab/V^2} \to \frac{V}{PV} = \frac{1}{P}$$

8. The cubic expansion coefficient is defined by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Calculate the cubic expansion and isothermal compressibility coefficients for an ideal gas.

Solution:

For an ideal gas V = nRT/P. The require partial derivatives are therefore:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \text{ and } \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

Using the definitions for  $\alpha$  and  $\kappa$  (using PV = nRT below):

$$\begin{aligned} \alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{PV} = \frac{nR}{nRT} = \frac{1}{T} \\ \kappa &= -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{nRT}{VP^2} = \frac{PV}{VP^2} = \frac{1}{P} \end{aligned}$$

9. A certain gas has the following equation of state:

$$P = \frac{nRT}{V - nb}$$

a) Calculate the following partial derivatives:

$$\left(\frac{\partial P}{\partial V}\right)_T$$
 and  $\left(\frac{\partial P}{\partial T}\right)_V$ 

b) Show that the following relation holds for the mixed partial derivatives for this equation of state:

$$\left(\frac{\partial^2 P}{\partial V \partial T}\right) = \left(\frac{\partial^2 P}{\partial T \partial V}\right)$$

Solution:

a)  

$$\left(\frac{\partial P}{\partial V}\right)_{T} = -\frac{nRT}{(V-nb)^{2}} \text{ and } \left(\frac{\partial P}{\partial T}\right)_{V} = \frac{nR}{V-nb}$$
b)  

$$\left(\frac{\partial^{2}P}{\partial V\partial T}\right) = -\frac{nR}{(V-nb)^{2}} \text{ and } \left(\frac{\partial^{2}P}{\partial T\partial V}\right) = -\frac{nR}{(V-nb)^{2}}$$

10. Calculate the compressibility factor Z for  $NH_3(g)$  at 400 K and 50 bar by using the attached graph and the virial equation. Solution:

By reading the value for B from the graph, using relation B' = B/RT, and the virial equation written in terms of P, we get:

$$Z = 1 + B'P + \dots = 1 + \frac{B}{RT}P + \dots$$
$$\approx 1 + \frac{(-100 \times 10^{-3} \text{ L mol}^{-1})}{(0.0831451 \text{ bar L K}^{-1} \text{ mol}^{-1})(400 \text{ K})} \times (50 \text{ bar}) = 0.85$$

