### Thermodynamics: Examples for chapter 5.

- 1. For the reaction  $N_2(g) + 3H_2(g) = 2NH_3(g)$ ,  $K = 1.60 \times 10^{-4}$  at 400 °C. Assume ideal gas behavior for the gases. Calculate:
  - (a)  $\Delta_r G^{\circ}$
  - (b)  $\Delta_r G$  when the partial pressures of N<sub>2</sub> and H<sub>2</sub> are maintained at 10.0 and 30.0 bar, respectively, and NH<sub>3</sub> is removed at a partial pressure of 3 bar.
  - (c) Is the reaction spontaneous under the latter conditions?

### Solution:

- (a) From the lecture notes:  $\Delta_r G^\circ = -RT \ln(K) = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (673 \text{ K}) \times \ln(1.60 \times 10^{-4}) = 48.9 \text{ kJ mol}^{-1}$
- (b) For ideal gases, we have  $a_i = f_i/P^\circ = P_i/P^\circ$  where  $P_i$  is the partial pressure of gas *i*. Using the lecture notes, we can write:

$$\Delta_r G = \Delta_r G^{\circ} + RT \ln \left( \prod_{i=1}^{N_S} a_i^{v_i} \right) = \Delta_r G^{\circ} + RT \ln \left( \frac{\left( P_{\rm NH_3} / P^{\circ} \right)^2}{\left( P_{\rm N_2} / P^{\circ} \right) \left( P_{\rm H_2} / P^{\circ} \right)^3} \right)$$
$$= (48.9 \text{ kJ mol}^{-1}) + (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (673 \text{ K}) \ln \left( \frac{3^2}{10 \times 30^3} \right)$$
$$= -8.78 \text{ kJ mol}^{-1}$$

- (c) Because  $\Delta_r G < 0$ , the reaction is spontaneous (i.e., proceeds from left to right).
- 2. At 55 °C and 1 bar the average molar mass of partially dissociated  $N_2O_4$  is 61.2 g mol<sup>-1</sup>. The molecular mass of pure  $N_2O_4$  is 92.01 g mol<sup>-1</sup>. Assume ideal gas behavior.
  - (a) Calculate the extent of reaction  $(\xi)$ .
  - (b) K for the reaction  $N_2O_4(g) = 2NO_2(g)$ .

(c) Calculate  $\xi$  at 55 °C if the total pressure is reduced to 0.1 bar.

### Solution:

(a) We can calculate the extent of reaction from the molar masses (see lecture notes):

$$\xi = \frac{M_1 - M_2}{M_2} = \frac{(92.01 \text{ g mol}^{-1}) - (61.2 \text{ g mol}^{-1})}{(61.2 \text{ g mol}^{-1})} = 0.503$$

(b) Based on the lecture notes, the equilibrium constant K is then:

$$K = \frac{4\xi^2 P/P^{\circ}}{1-\xi^2} = \frac{4 \times (0.503)^2 \times (1)}{1-(0.503)^2} = 1.36$$

(c) The equilibrium constant K does not depend on pressure, only on temperature (which is the same as above). Thus we can use the same equation again but this time solve for  $\xi$ :

$$K = \frac{4\xi^2 \times 0.1}{1 - \xi^2} = 1.36 \Rightarrow \xi \approx 0.879 \text{ (the other root is negative)}$$

3. Express K for the reaction:  $CO(g) + 3H_2(g) = CH_4(g) + H_2O(g)$  in terms of the equilibrium extent of the reaction  $\xi_{eq}$  when one mole of CO is mixed with one mole of hydrogen. Assume ideal gas behavior. Solution:

We can write the partial pressures  $P_i$  using the molar fractions as  $P_i = y_i P$ . Entering these partial pressures into the expression for the equilibrium constant K, we get  $(\xi = \xi_{eq})$ :

$$K = \frac{\left(\frac{\xi}{2-2\xi}\right)\left(\frac{P}{P^{\circ}}\right)\left(\frac{\xi}{2-2\xi}\right)\left(\frac{P}{P^{\circ}}\right)}{\left(\frac{1-\xi}{2-2\xi}\right)\left(\frac{P}{P^{\circ}}\right)\left(\frac{1-3\xi}{2-2\xi}\right)^{3}\left(\frac{P}{P^{\circ}}\right)^{3}} = \frac{\xi^{2}\left(2-2\xi\right)^{2}}{\left(1-\xi\right)\left(1-3\xi\right)^{3}\left(P/P^{\circ}\right)^{2}}$$

- 4. At 1273 K and at a total pressure of 30.4 bar the equilibrium in the reaction  $CO_2(g)+C(s) = 2CO(g)$  is such that 17 mol % of the gas is  $CO_2$ . Assume ideal behavior for gases and activities for solids can be taken to be one.
  - (a) What percentage would be  $CO_2$  if the total pressure were 20.3 bar?
  - (b) What would be the effect on the equilibrium of adding  $N_2$  to the reaction mixture in a closed vessel until the partial pressure of  $N_2$  is 10 bar?
  - (c) At what pressure of the reactants will 25% of the gas be  $CO_2$ ?

## Solution:

(a) First calculate the partial pressures and the equilibrium constant under the known conditions (activity of pure solid is one):

$$P_{\rm CO_2} = (30.4 \text{ bar}) \times (17\%) = 5.2 \text{ bar}$$
$$P_{\rm CO} = (30.4 \text{ bar}) \times (83\%) = 25.2 \text{ bar}$$
$$K = \frac{(P_{\rm CO}/P^\circ)^2}{(P_{\rm CO_2}/P^\circ)} = \frac{(25.2)^2}{5.2} = 122$$

Let  $\xi$  be the extent of reaction. The amount of  $CO_2(g)$  is given by  $1 - \xi$  and CO(g) by  $2\xi$ . The mole fractions as a function of  $\xi$ are then:

$$y_{\rm CO_2} = \frac{1-\xi}{1+\xi}$$
 and  $y_{\rm CO} = \frac{2\xi}{1+\xi}$ 

Since we have ideal gases, the partial pressures are given by  $P_{\rm CO_2} = y_{\rm CO_2}P$  and  $P_{\rm CO} = y_{\rm CO}P$ . By inserting these into the expression for the equilibrium constant, we get (activity of the solid is one):

$$K = \frac{\left(P_{\rm CO}/P^{\circ}\right)^2}{\left(P_{\rm CO_2}/P^{\circ}\right)} = \left(\frac{P}{P^{\circ}}\right) \times \frac{4\xi^2}{1-\xi^2}$$

Since K = 122 and  $P/P^{\circ} = 20.3$ , we can calculate  $\xi = 0.77$ . When this is inserted into the expression for CO<sub>2</sub> molar fraction above, we get  $y_{\rm CO_2} = 0.13$ . Thus 13% of CO<sub>2</sub> at 20.3 bar.

- (b) This does not affect the reaction at all as the partial pressures of the components do not change. If the volume would change then this would affect the reaction.
- (c) If 25% is CO<sub>2</sub> then the rest is CO (75%). This gives:

$$K = \frac{(0.75 (P/P^{\circ}))^2}{0.25 (P/P^{\circ})} \Rightarrow P = 54 \text{ bar}$$

5. The following reaction is nonspontaneous at room temperature and endothermic:

$$3C(\text{graphite}) + 2H_2O(g) = CH_4(g) + 2CO(g)$$

As the temperature is raised, the equilibrium constant will become equal to unity at some point. Estimate this point using the data given below (in units of kJ mol<sup>-1</sup>). Finally, use the van't Hoff equation with assumption that  $\Delta_r H^{\circ}$  is independent of temperature to get a better estimate for this temperature. At 1000 K,  $\Delta_r H^{\circ} = 181.90$  kJ mol<sup>-1</sup>.

$T(\mathbf{K})$	$\Delta_f G^{\circ}(\mathrm{CH}_4(g))$	$\Delta_f G^{\circ}(\mathrm{CO}(g))$	$\Delta_f G^{\circ}(\mathrm{H}_2\mathrm{O}(g))$	$\Delta_f G^{\circ}(\mathbf{C}(s))$
0	-66.911	-113.805	-238.921	0.000
298	-50.768	-137.163	-228.582	0.000
500	-32.741	-155.414	-219.051	0.000
1000	19.492	-200.275	-192.590	0.000
2000	130.802	-286.034	-135.528	0.000
3000	242.332	-367.816	-77.163	0.000

Solution:

First we calculate  $\Delta_r G^\circ$  from the given  $\Delta_f G^\circ$  values:

$$\Delta_r G^{\circ} = \Delta_f G^{\circ}(\mathrm{CH}_4(g)) + 2\Delta_f G^{\circ}(\mathrm{CO}(g)) - 2\Delta_f G^{\circ}(\mathrm{H}_2\mathrm{O}(g)) - \Delta_f G^{\circ}(\mathrm{C}(s))$$

This can be related to the equilibrium constant K:

$$K = \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) = \exp\left(-\frac{4.122 \text{ kJ mol}^{-1}}{\left(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}\right)(1000 \text{ K})}\right)$$
$$= 0.609$$

Next we integrate the van't Hoff equation:

$$\left(\frac{d\ln(K)}{dT}\right) = \frac{\Delta_r H^{\circ}}{RT^2} \Rightarrow \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Inserting the values:  $K_2 = 1$ ,  $K_1 = 0.609$ ,  $T_2$  =unknown, and  $T_1 = 1000$  K. Solving for  $T_2$  gives an estimate  $T_2 = 1023$  K.

6. Starting with the fundamental equation for G in the form:  $dG = -SdT + VdP + \Delta_r Gd\xi$ , derive equations for calculating  $\Delta_r S$ ,  $\Delta_r V$  and  $\Delta_r H$  in terms of  $\Delta_r G(P, T)$  for a chemical reaction. Hint: Use the Maxwell relations.

Solution:

First we note that this equation is very similar to that given in the lecture notes (see the Maxwell equations). Now  $\Delta_r G$  corresponds to  $\mu_i$  and  $\xi$  to  $n_i$ :

$$\underbrace{-\left(\frac{\partial S}{\partial \xi}\right)_{T,P}}_{=\Delta_r S} = \left(\frac{\partial \left(\Delta_r G\right)}{\partial T}\right)_{\xi,P} \text{ and } \underbrace{\left(\frac{\partial V}{\partial \xi}\right)_{T,P}}_{=\Delta_r V} = \left(\frac{\partial \left(\Delta_r G\right)}{\partial P}\right)_{\xi,T}$$

Thus by calculating derivatives of the reaction Gibbs energy with respect to temperature and pressure, we can obtain values for  $\Delta_r S$  and  $\Delta_r V$ .  $\Delta_r H$  is directly given by:  $\Delta_r H = \Delta_r G - T (\partial \Delta_r G / \partial T)_P$ .

7. Consider decomposition of silver oxide:  $2Ag_2O(s) = 4Ag(s)+O_2(g)$ . For  $Ag_2O(s)$ ,  $\Delta_f H^\circ = -31.05$  kJ mol<sup>-1</sup> and  $\bar{S}^\circ = 121.3$  kJ K<sup>-1</sup> mol<sup>-1</sup>, and assume that  $\Delta_r C_P^\circ = 0$ . Calculate the temperature at which the equilibrium pressure of  $O_2$  is 0.2 bar. This temperature is of interest because  $Ag_2O$  will decompose to yield Ag(s) at temperatures above this value if it is in contact with air. Assume that  $O_2$  follows the ideal gas law and that the activities of solid reagents are one.

### Solution:

Recall that at equilibrium  $\Delta_r G = 0$  and then  $0 = \Delta_r G = \Delta_r G^\circ + RT \ln (P/P^\circ)$ . Note that only  $O_2(g)$  enters the equation as the other components are solids and have unit activities. On the other hand,  $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ . Combining the two equations and solving for T gives:

$$T = \frac{\Delta_r H^{\circ}}{\Delta_r S^{\circ} - R \ln\left(P/P^{\circ}\right)}$$

To use this result, we need to know  $\Delta_r H^{\circ}$  and  $\Delta_r S^{\circ}$  at temperature T. Provided that  $\Delta_r C_P = 0$ , both of these quantities are independent temperature (see lecture notes). The reaction enthalpy is then given by (note that all other  $\Delta_f H^{\circ}$  are zero except for Ag<sub>2</sub>O(s)):

$$\Delta_r H^{\circ} = \sum_i v_i \Delta_f H^{\circ} = -2 \left(-31.05 \text{ kJ mol}^{-1}\right) = 62.10 \text{ kJ mol}^{-1}$$
$$\Delta_r S^{\circ} = \sum_i v_i \bar{S}^{\circ} = 4 \times \left(42.55 \text{ JK}^{-1} \text{mol}^{-1}\right) + \left(205.138 \text{ JK}^{-1} \text{mol}^{-1}\right)$$
$$-2 \times \left(121.3 \text{ JK}^{-1} \text{mol}^{-1}\right) = 132.7 \text{ JK}^{-1} \text{ mol}^{-1}$$

When these numbers are inserted into the earlier expressions, we get:

$$T = \frac{(62100 \text{ J mol}^{-1})}{(132.7 \text{ JK}^{-1} \text{mol}^{-1}) - (8.314 \text{ JK}^{-1} \text{mol}^{-1}) \ln(0.2)} = 425 \text{ K}$$

8. The reaction  $2\text{NOCl}(g) = 2\text{NO}(g) + \text{Cl}_2(g)$  comes to equilibrium at 1 bar total pressure and 227 °C when the partial pressure of the nitrosyl chloride (NOCl) is 0.64 bar. Only NOCl was present initially. Assume ideal gas behavior.

(a) Calculate  $\Delta_r G^{\circ}$  for this reaction.

(b) At what total pressure will the partial pressure of  $Cl_2$  be 0.1 bar?

Solution:

(a) Init.  $n_0$  NOCl NO Cl<sub>2</sub> Total Eq.  $n_0 - 2\xi$   $\xi$   $n_0 + \xi$ 

Here  $\xi$  goes from 0 to  $n_0/2$ . It is more convenient to work with reduced variable  $\xi' = \xi/n_0$ . In this case the above table takes the form:

	NOCl	NO	$Cl_2$	Total
Init.	1	0	0	1
Eq.	$1 - 2\xi'_{eq}$	$2\xi'_{eq}$	$\xi'_{eq}$	$1 + \xi'_{eq}$
$y_i$	$(1 - 2\xi')/(1 + \xi')$	$2\xi'/(1+\xi')$	$\xi'/(1+\xi')$	1

Calculation with both  $\xi$  and  $\xi$  would give the same molar fractions and hence the same equilibrium constant K. At equilibrium  $P_{tot} =$ 1 bar and  $P_{\text{NOCl}} = 0.64$  bar. Because  $P_{\text{NOCl}} = y_{\text{NOCl}}P_{tot}$ , we get  $y_{\text{NOCl}} = 0.64$ . Above we have an expression that relates  $y_{\text{NOCl}}$  and  $\xi'$  to each other:

$$y_{\text{NOCl}} = \frac{1 - 2\xi'_{eq}}{1 + \xi'_{eq}} = 0.64 \Rightarrow \xi'_{eq} = 0.136$$

The equilibrium constant can be written in terms of molar fractions to yield K ( $y_{\text{Cl}_2}^{eq} = 0.120$  and  $y_{\text{NO}}^{eq} = 0.239$ ):

$$K = \frac{\left(P_{\rm NO}^{eq}\right)^2 \left(P_{\rm Cl_2}^{eq}\right)}{\left(P_{\rm NOCl}^{eq}\right)^2} = \frac{\left(y_{\rm NO}^{eq}\right)^2 \left(y_{\rm Cl_2}^{eq}\right)}{\left(y_{\rm NOCl}^{eq}\right)^2} \times \left(\frac{P_{tot}}{P^{\circ}}\right) = 0.0167$$

Now K can be related to  $\Delta_r G^\circ$ :

$$\Delta_r G^\circ = -RT \ln(K) = -(8.314 \text{JK}^{-1} \text{mol}^{-1}) \times (500 \text{ K}) \ln(0.0167)$$
$$= 17.0 \text{ kJ mol}^{-1}$$

(b) Note here that a change in total pressure will change the extent of reaction. For this reason, we have to solve for both  $\xi'$  and  $P_{tot}$  at the same time by using two different equations:

$$K = \frac{\left(y_{\text{NO}}^{eq}\right)^2 \left(y_{\text{Cl}_2}^{eq}\right)}{\left(y_{\text{NOCl}}^{eq}\right)^2} \times \left(\frac{P_{tot}}{P^\circ}\right) = 0.0167$$
$$y_{\text{Cl}_2}^{eq} \times P_{tot} = 0.1 \text{ bar}$$

Inserting the 2nd into the 1st gives:

$$\frac{(y_{\rm NO}^{eq})^2 \times \left(\frac{0.1 \text{ bar}}{1 \text{ bar}}\right)}{(y_{\rm NOCl}^{eq})^2} = 0.0167 \Rightarrow \frac{y_{\rm NO}^{eq}}{y_{\rm NOCl}^{eq}} = \sqrt{0.167}$$
$$\frac{2\xi_{eq}'}{1 - 2\xi_{eq}'} = 0.409 \Rightarrow \xi_{eq}' = 0.145 \Rightarrow y_{\rm Cl_2}^{eq} = \frac{0.145}{1 + 0.145} = 0.127$$
$$\Rightarrow P_{tot} = 0.787 \text{ bar}$$

9. For a chemical reaction,  $\ln(K) = a + b/T + c/T^2$ . Derive the corresponding expressions to calculate  $\Delta_r G^{\circ}$ ,  $\Delta_r H^{\circ}$ ,  $\Delta_r S^{\circ}$ , and  $\Delta_r C_P^{\circ}$ . Solution:

By using the equations in the lecture notes, we can write:

$$\Delta_r G^\circ = -RT \ln(K) = -R \left( aT + b + c/T \right)$$
$$\Delta_r H^\circ = -T^2 \left( \frac{d \left( \Delta_r G^\circ / T \right)}{dT} \right) = RT^2 \left( \frac{d \ln(K)}{dT} \right) = -R \left( b + \frac{2c}{T} \right)$$
$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = R \left( a - \frac{c}{T^2} \right)$$

From the following, we can solve for  $\Delta_r C_P^{\circ}$  after differentiation with respect to T:

$$\Delta_r H^{\circ}(T) = \Delta_r H^{\circ}(298.15 \text{ K}) + \int_{298.15 \text{ k}}^T \Delta_r C_P^{\circ} dT'$$

$$\Rightarrow \Delta_r C_P^\circ = \frac{d \left( \Delta_r H^\circ \right)}{dT} = 2Rc/T^2$$

10. The equilibrium constant for the association of benzoic acid to a dimer in dilute benzene solutions is as follows at 43.9 °C:  $2C_6H_5COOH=$  $(C_6H_5COOH)_2$  with  $K_c = 2.7 \times 10^2$ . Note that molar concentrations were used in expressing the equilibrium constant. Calculate  $\Delta_r G^{\circ}$  and state its meaning. Hint: In dilute solutions activities can be replaced by concentrations.

# Solution:

Since concentrations and activities are equal in dilute solutions,  $K_c$  can be directly applied in calculating  $\Delta_r G^\circ$ :

$$\Delta_r G^\circ = -RT \ln (K_c) = - (8.315 \text{ JK}^{-1} \text{ mol}^{-1}) (317 \text{ K}) \ln (2.7 \times 10^2)$$
$$= -14.8 \text{ kJ mol}^{-1}$$