

10.34 – Fall 2006

Homework #7

Due Date: Wednesday, October 25th, 2006 – 9 AM

Problem 1:

Do problem 4.B.1 in Beers' textbook (pg. 294).

Problem 2:

Do problem 5.B.4 in Beers' textbook (pg. 357).

Problem 3: *Equilibrium on a mixture of gases*

In this problem, we want to find the equilibrium composition of a mixture of gases at constant $T = 1000\text{ K}$ and $P = 1\text{ atm}$ in the steam reforming of methane:



If you wanted to know the best you can do for hydrogen production, you would need to know the equilibrium composition at the temperature of interest. The typical solution procedure to this type of problem involves minimizing the total Gibbs free energy of the system by changing the number of moles of the species in the system, subject to the conservation of atoms.

We can write that the Gibbs free energy of the system is a function of T, P, and the number of moles of the species, then differentiate to get the following:

$$G_{total} = G_{total}(T, P, n_i)$$
$$dG_{total} = \left(\frac{\partial G_{total}}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G_{total}}{\partial P} \right)_{T, n_i} dP + \sum_{species} \left(\frac{\partial G_{total}}{\partial n_i} \right)_{T, n_{k \neq i}} dn_i$$

Since we are dealing with a constant T and P system, the first two terms vanish:

$$dG_{total} = \sum_{species} \left(\frac{\partial G_{total}}{\partial n_i} \right)_{T, n_{k \neq i}} dn_i = \sum_{species} \mu_i dn_i$$

If you realize that the right hand side can also be expanded as:

$$dG_{total} = \sum_{species} \mu_i dn_i = \sum_{species} \mu_i dn_i + n_i d\mu_i - n_i d\mu_i = \sum_{species} d(n_i \mu_i) - n_i d\mu_i$$

And you also use the equilibrium Gibbs-Duhem relation as constant T and P to realize:

$$0 = -\underline{S} \cdot dT + \underline{V} \cdot dP - \sum_{species} n_i \cdot d\mu_i \xrightarrow{\text{const. } T \text{ and } P} 0 = \sum_{species} n_i \cdot d\mu_i$$

This then results in the following:

$$dG_{total} = \sum_{species} d(n_i \mu_i) \xrightarrow{\text{Integrate}} G_{total} = \sum_{species} n_i \mu_i$$

Therefore, for a single phase system, the total Gibbs free energy can be written in terms of chemical potential of each species:

$$G_{total} = \sum_{species} n_i \left(\frac{\partial G_{total}}{\partial n_i} \right)_{T,P,n_k} = \sum_{species} n_i \mu_i$$

The chemical potential of a species can generally be written as the following:

$$\mu_i = G_i^\circ + RT \ln \left(\frac{\hat{f}_i}{f_i^\circ} \right) = G_i^\circ + RT \ln \left(\frac{y_i \hat{\phi}_i P}{P^\circ} \right) \xrightarrow{\text{ideal, 1atm}} \boxed{\mu_i = G_i^\circ + RT \ln \left(\frac{n_i}{N_{total}} \right)}$$

We now have a framework to determine the equilibrium conditions by solving the following optimization problem:

$$\begin{aligned} \min_{\underline{n}} \quad & G_{total}(\underline{n}) \\ \text{s.t.} \quad & \underline{A}_{eq} \cdot \underline{n} = \underline{b}_{eq} \\ & \underline{A} \cdot \underline{n} \leq \underline{b} \end{aligned}$$

Question:

In this problem, we want to find the equilibrium number of moles and mole fraction for the following species in the steam reforming system: CH₄, H₂O, CO, CO₂, HO₂, H₂, and HOOH. The Gibbs free energy values at 1000 K and 1 atm are (in J/mole):

$$\begin{array}{lll} G_{CH_4} = 19720 & G_{H_2O} = -192420 & G_{CO} = -200240 \\ G_{CO} = -395790 & G_{HO_2} = -227000 & G_{H_2} = 0 & G_{HOOH} = -369060 \end{array}$$

Part A:

Consider a constant T and P equilibrium reactor, with T = 1000 K and P = 1 atm. The initial charge of reactants is: 2 moles CH₄, 3 moles H₂O, 0.5 moles CO, and 1 mole of H₂. Give the number of moles of each species at equilibrium, as well as the corresponding mole fraction.

Part B:

The species HO₂ is a radical species and would typically be found in very small quantities. What would be the approximate number of moles at equilibrium for HO₂ estimated using the concentrations of the major species? Does the value found using the minimization make sense, explain?