Chapter 13

Problem 13.1

Develop expressions for the mole fractions of reacting species as functions of the reaction coordinate for:

(a) A system containing 2 mol NH_3 and 5 mol O_2 and undergoing the reaction:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

(b) A system initially containing 3 mol H_2S and 5 mol O_2 and undergoing the reaction:

$$2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(g) + 2\,SO_2(g)$$

(c) A system containing 3 mol NO_2, 4 mol NH_3, and 1 mol N_2 and undergoing the reaction:

$$6\,NO_2(g) + 8\,NH_3(g) \longrightarrow 7\,N_2(g) + 12\,H_2O(g)$$

Solution

The solution here is to substitute into Eq. (13.5)

$$y_i = \frac{n_{io} + \nu_i \varepsilon}{n_0 + \nu \varepsilon} \tag{13.5}$$

(a)

$$\boxed{\begin{aligned} y_{NH_3} &= \frac{2 - 4\varepsilon}{7 + \varepsilon} \\ y_{O_2} &= \frac{5 - 5\varepsilon}{7 + \varepsilon} \end{aligned}}$$

(b)

$$\boxed{\begin{aligned} y_{H_2S} &= \frac{3 - 2\varepsilon}{8 - \varepsilon} \\ y_{O_2} &= \frac{5 - 3\varepsilon}{8 - \varepsilon} \end{aligned}}$$

(c)

$$\boxed{\begin{aligned} y_{NO_2} &= \frac{3 - 6\varepsilon}{8 + 5\varepsilon} \\ y_{NH_3} &= \frac{4 - 8\varepsilon}{8 + 5\varepsilon} \\ y_{N_2} &= \frac{1 + 7\varepsilon}{8 + 5\varepsilon} \end{aligned}}$$

Problem 13.2

A system initially containing 2 mol C_2H_4 and 3 mol O_2 undergoes the reactions:

$$C_2H_4(g) + \frac{1}{2}O_2(g) \longrightarrow ((CH_2)_2)O(g)$$
$$C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$$

Develop expressions for the mole fractions of the reacting species as functions of the reaction coordinates for the two reactions.

Solution

The two chemical reactions need to be added and the same solution in Problem 13.1 is to be used.

$$2\,C_2H_4(g) + 3.5\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g) + ((CH_2)_2)O(g)$$

$$\boxed{\begin{aligned} y_{C_2H_4} &= \frac{2-2\varepsilon}{5} \\ y_{O_2} &= \frac{3-3.5\varepsilon}{5} \end{aligned}}$$

Problem 13.3

A system formed initially of 2 mol CO_2, 5 mol H_2, and 1 mol CO undergoes the reactions:

$$\begin{aligned} CO_2(g) + 3\,H_2(g) &\longrightarrow CH_3OH(g) + H_2O(g) \\ CO_2(g) + H_2(g) &\longrightarrow CO(g) + H_2O(g) \end{aligned}$$

Develop expressions for the mole fractions of the reacting species as functions of the reaction coordinates for the two reactions.

Solution

Similar to the previous problem.

$$2\,CO_2(g) + 4\,H_2(g) \longrightarrow CH_3OH(g) + 2\,H_2O(g) + CO(g)$$

$$\boxed{\begin{aligned} y_{CO_2} &= \frac{2-2\varepsilon}{8-2\varepsilon} \\ y_{H_2} &= \frac{5-4\varepsilon}{8-2\varepsilon} \\ y_{CO} &= \frac{1+\varepsilon}{8-2\varepsilon} \end{aligned}}$$

Problem 13.4

Consider the water-gas-shift reaction:

$$H_2(g) + CO_2(g) \longrightarrow H_2O(g) + CO(g)$$

At high temperatures and low to moderate pressures the reacting species form an ideal-gas mixture. By Eq. (11.27):

$$G = \sum_i y_i G_i + RT \sum_i y_i \ln y_i$$

When the Gibbs energies of the elements in their standard states are set equal to zero, $G_i = \Delta G^\circ_{f_i}$, for each species, and then:

$$G = \sum_i y_i \Delta G^\circ_{f_i} + RT \sum_i y_i \ln y_i \tag{A}$$

At the beginning of Sec. 13.2 we noted that Eq. (14.68) is a criterion of equilibrium. Applied to the water-gas-shift reaction with the understanding that T and P are constant, this equation becomes:

$$dG' = d(nG) = ndG + Gdn = 0 \qquad n\frac{dG}{d\varepsilon} + G\frac{dn}{d\varepsilon} = 0$$

Here, however, $dn/d\varepsilon = 0$. The equilibrium criterion therefore becomes:

$$\frac{dG}{d\varepsilon} = 0 \tag{B}$$

Once the y_i are eliminated in favor of ε, Eq. (A) relates G to ε. Data for $\Delta G^\circ_{f_i}$ for the compounds of interest are givent with Ex. 13.13. For a temperature of 1000 K (the reaction is unaffected by P) and for a feed of 1 mol H_2 and 1 mol CO_2:

(a) Determine the equilibrium value of ε by application of Eq. (B).

(b) Plot G vs. ε, indicating the location of the equilibrium value of ε determined in (a).

Solution

(a) Solving for ε:

$$y_{H_2} = y_{CO_2} = \frac{1-\varepsilon}{2}$$
$$y_{H_2O} = y_{CO} = \frac{\varepsilon}{2}$$

From Eq. (A)—the values of $\Delta G^\circ_{f_i}$ in J mol^{-1} are given in Example 13.13:

$$G = \left(\frac{1-\varepsilon}{2}\right)(-395790) + \left(\frac{\varepsilon}{2}\right)(-200240 - 192420) + R(1000)\left[2\left(\frac{1-\varepsilon}{2}\right)\ln\left(\frac{1-\varepsilon}{2}\right) + 2\left(\frac{\varepsilon}{2}\right)\ln\left(\frac{\varepsilon}{2}\right)\right]$$

Differentiate with respect to ε and solve for the root as in Eq. (B):

$$\boxed{\varepsilon = 0.452}$$

(b) See Figure 1

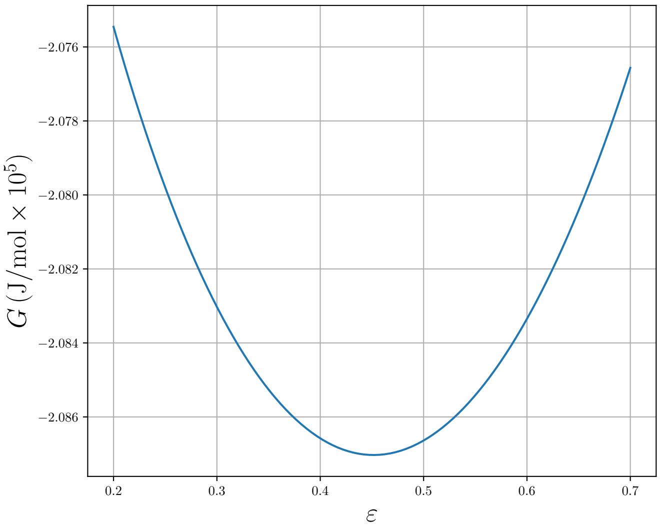

Figure 1: The graph of G with respect to ε for the system described in 13.4

Problem 13.5

Rework Pb. 13.4 for a temperature of:

(a) 1100 K;

(b) 1200 K;

(c) 1300 K.

Solution

Refer to Pb. 13.4 for the solution. The plots of (a), (b), and (c) are shown in Figure 2

(a) $\boxed{\varepsilon = 0.456}$

(a) $\boxed{\varepsilon = 0.460}$

(a) $\boxed{\varepsilon = 0.463}$

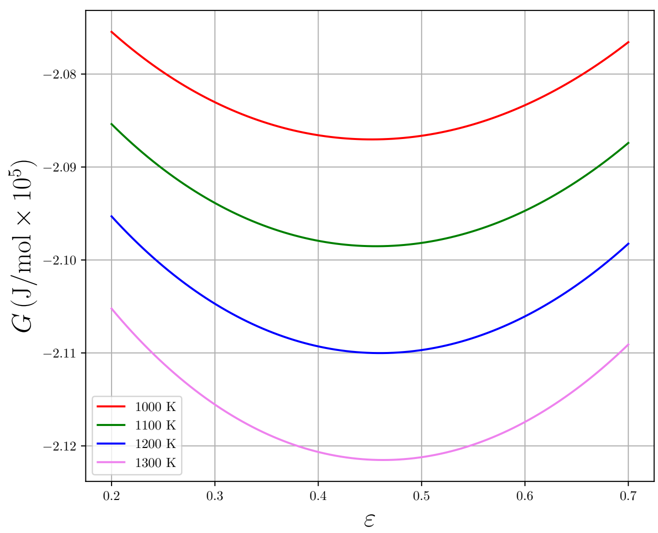

Figure 2: The graph of G with respect to ε for the systems described in 13.5