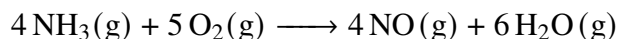# Chapter 13

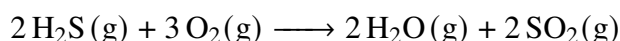## Problem 13.1

Develop expressions for the mole fractions of reacting species as functions of the reaction coordinate for:
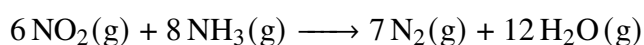
(a) A system containing 2 mol NH_3 and 5 mol O_2 and undergoing the reaction:

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

(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)

$$y_i = \frac{n_{io} + \nu_i \varepsilon}{n_0 + \nu \varepsilon} \qquad (13.5)$$

(a)

$$y_{NH_3} = \frac{2 - 4\varepsilon}{7 + \varepsilon}$$
$$y_{O_2} = \frac{5 - 5\varepsilon}{7 + \varepsilon}$$

(b)

$$y_{H_2S} = \frac{3 - 2\varepsilon}{8 - \varepsilon}$$
$$y_{O_2} = \frac{5 - 3\varepsilon}{8 - \varepsilon}$$

(c)

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

Problem 13.2

A system initially containing 2 mol C_2H_4 and 3 mol O_2 undergoes the reactions:
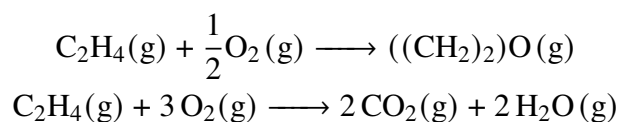
$$C_2H_4(g) + \frac{1}{2}O_2(g) \longrightarrow ((CH_2)_2)O(g)$$
$$C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$$

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

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

$$y_{C_2H_4} = \frac{2 - 2\varepsilon}{5}$$

$$y_{O_2} = \frac{3 - 3.5\varepsilon}{5}$$

Problem 13.3

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

$$CO_2\,(g) + 3\,H_2\,(g) \longrightarrow CH_3OH\,(g) + H_2O\,(g)$$
$$CO_2\,(g) + H_2\,(g) \longrightarrow CO\,(g) + H_2O\,(g)$$

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

Solution

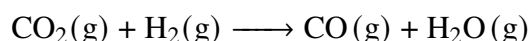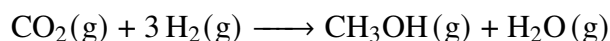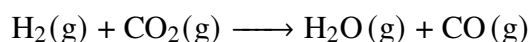Similar to the previous problem.

$$2\,CO_2\,(g) + 4\,H_2\,(g) \longrightarrow CH_3OH\,(g) + 2\,H_2O\,(g) + CO\,(g)$$
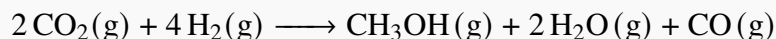
$$y_{CO_2} = \frac{2 - 2\varepsilon}{8 - 2\varepsilon}$$

$$y_{H_2} = \frac{5 - 4\varepsilon}{8 - 2\varepsilon}$$

$$y_{CO} = \frac{1 + \varepsilon}{8 - 2\varepsilon}$$

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:

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

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:

$$\frac{dG}{d\varepsilon} = 0 \qquad (B)$$

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)

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

$$y_{H_2O} = y_{CO} = \frac{\varepsilon}{2}$$

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

$$G = \left(\frac{1-\varepsilon}{2}\right)(-395790) + \left(\frac{\varepsilon}{2}\right)(-200240 - 192420) +$$

$$R(1000)\left[2\left(\frac{1-\varepsilon}{2}\right)\ln\left(\frac{1-\varepsilon}{2}\right)\right] + \left[2\left(\frac{\varepsilon}{2}\right)\ln\left(\frac{\varepsilon}{2}\right)\right]$$

Differentiate with respect to ε and equate to zero as in Eq. (B):

$$\frac{dG}{d\varepsilon} = 0 = -\frac{1}{2}(-395790) + \frac{1}{2}(-200240 - 192420) +$$