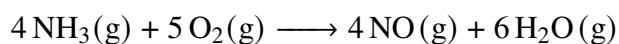# Chapter 13
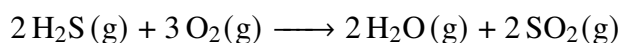
Problem 13.1

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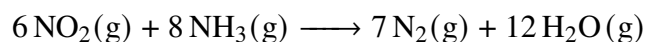
(a) A system containing 2 mol NH_3 and 5 mol O_2 and undergoing the reaction:

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

(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)
>
> $$y_i = \frac{n_{io} + v_i\varepsilon}{n_0 + v\varepsilon} \tag{13.5}$$
>
> (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:
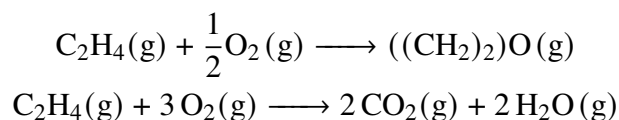
$$C_2H_4(g) + \frac{1}{2}O_2(g) \longrightarrow ((CH_2)_2)O(g)$$

$$C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$$

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

> **Solution**
>
> Two extents, ε_1 and ε_2 are to be considered:
>
> $$y_{C_2H_4} = \frac{2 - \varepsilon_1 - \varepsilon_2}{5 - 1/2\varepsilon_1}$$
>
> $$y_{O_2} = \frac{3 - 1/2\varepsilon_1 - 3\varepsilon_2}{5 - 1/2\varepsilon_1}$$

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.
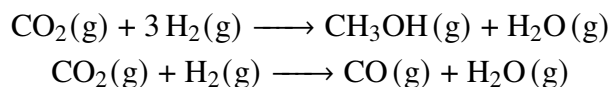
> **Solution**
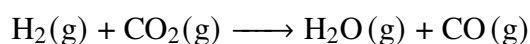>
> Similar to the previous problem.
>
> $$y_{CO_2} = \frac{2 - \varepsilon_1 - \varepsilon_2}{8 - 2\varepsilon_1}$$
>
> $$y_{H_2} = \frac{5 - 3\varepsilon_1 - \varepsilon_2}{8 - 2\varepsilon_1}$$
>
> $$y_{CO} = \frac{1 + \varepsilon_2}{8 - 2\varepsilon_1}$$

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):

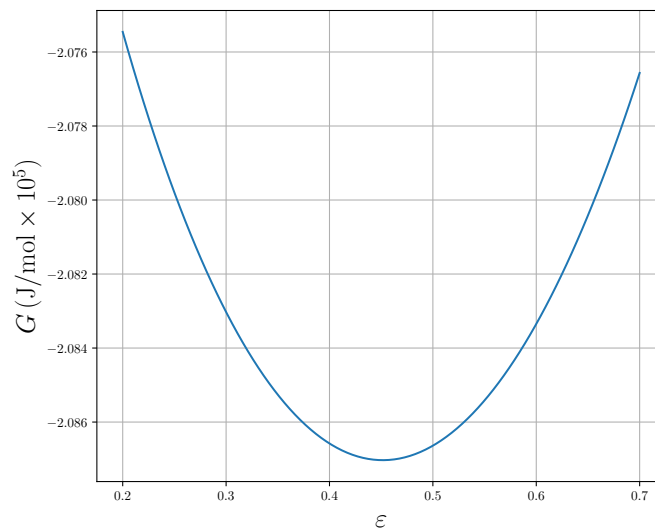$$\boxed{\varepsilon = 0.452}$$

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

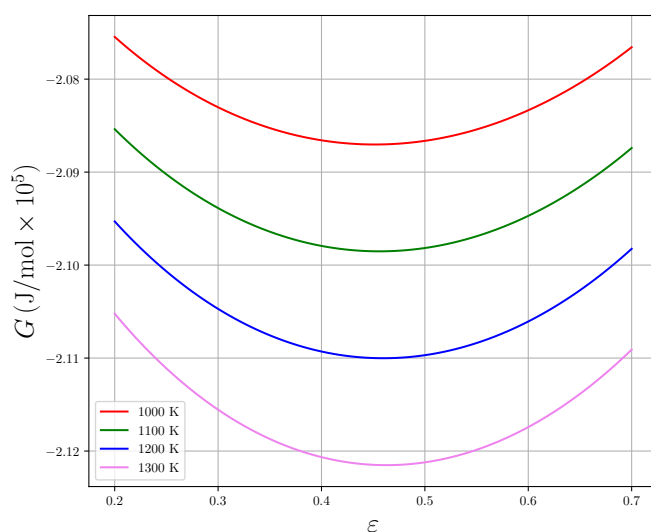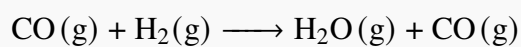(b) $\boxed{\varepsilon = 0.460}$

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

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

Problem 13.6

Use the method of equilibrium constants to verify the value of ε found as an answer in one of the following:

(a) Pb. 13.4;

(b) Pb. 13.5(a);

(c) Pb. 13.5(b);

(d) Pb. 13.5(c).

> **Solution**
>
> $$CO(g) + H_2(g) \longrightarrow H_2O(g) + CO(g)$$
>
> $$y_{H_2} = y_{CO_2} = \frac{1 - \varepsilon}{2}$$
>
> $$y_{CO_2} = y_{H_2O} = \frac{\varepsilon}{2}$$
>
> $$K = \frac{y_{H_2O}\, y_{CO}}{y_{H_2}\, y_{CO}} = \left(\frac{\varepsilon}{1 - \varepsilon}\right)^2$$
>
> $$K = \exp\left(\frac{-\Delta G}{RT}\right)$$
>
> $$\varepsilon = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

$$\varepsilon = \begin{bmatrix} 0.4531 \\ 0.5021 \\ 0.5399 \\ 0.5709 \end{bmatrix}$$

Problem 13.7

Develop a general equation for the standard Gibbs-energy change of reaction ΔG° as a function of temperature for one of the reactions given in parts (a), (f), (i), (n), (r), (t), (u), (x), and (y) of Pb. 4.21.
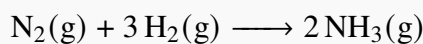

Solution

Write ΔG_r° in terms of K and T:
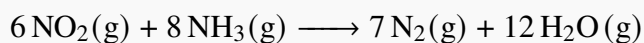
$$K = e^{-\Delta G_r^\circ/(RT)}$$
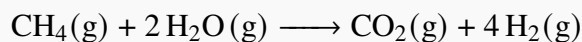
$$\Delta G_r^\circ = RT \ln\left(\frac{1}{K}\right)$$

(a)

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

$$\boxed{\Delta G_r^\circ = RT \ln\left(\frac{y_{N_2} y_{H_2}^2}{y_{NH_3}^2}\right)}$$

(f)

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

$$\boxed{\Delta G_r^\circ = RT \ln\left(\frac{y_{NO_2}^6 y_{NH_3}^8}{y_{N_2}^7 y_{H_2O}^{12}}\right)}$$

(i)

$$CH_4(g) + 2\,H_2O(g) \longrightarrow CO_2(g) + 4\,H_2(g)$$

$$\boxed{\Delta G_r^\circ = RT \ln\left(\frac{y_{CH_4} y_{H_2O}^2}{y_{CO_2} y_{H_2}^4}\right)}$$

(n)

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$$

$$\boxed{\Delta G_r^\circ = RT \ln\left(\frac{y_{N_2} y_{O_2}}{y_{NO}^2}\right)}$$

(r)

$$CH_3CHO(g) + H_2(g) \longrightarrow C_2H_5OH(g)$$
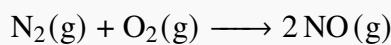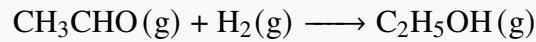
$$\Delta G_r^\circ = RT \ln\left(\frac{y_{CH_3CHO} y_{H_2}}{y_{C_2H_5OH}}\right)$$

(t)

$$C_2H_5CH=CH_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_2=CHCH=CH_2(g) + H_2O(g)$$
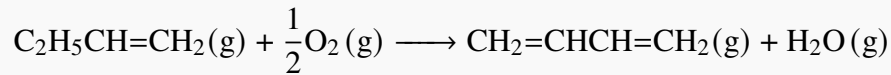
$$\Delta G_r^\circ = RT \ln\left(\frac{y_{C_2H_5CH=CH_2} y_{O_2}^{1/2}}{y_{CH_2=CHCH=CH_2} y_{H_2O}}\right)$$

(u)

$$C_4H_{10}(g) \longrightarrow CH_2=CHCH=CH_2(g) + 2H_2(g)$$

$$\Delta G_r^\circ = RT \ln\left(\frac{y_{C_4H_{10}}}{y_{CH_2=CHCH=CH_2} y_{H_2}^2}\right)$$

(x)

$$N_2(g) + C_2H_2(g) \longrightarrow 2HCN(g)$$

$$\Delta G_r^\circ = RT \ln\left(\frac{y_{N_2} y_{C_2H_2}}{y_{HCN}^2}\right)$$

(y)

$$C_6H_5 \cdot C_2H_5(g) \longrightarrow C_6H_5CH=CH_2(g) + H_2(g)$$
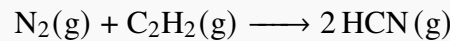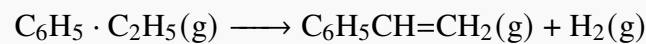
$$\Delta G_r^\circ = RT \ln\left(\frac{y_{C_6H_5 \cdot C_2H_5}}{y_{C_6H_5CH=CH_2} y_{H_2}}\right)$$

Problem 13.11

The following reaction reaches equilibrium at 500 °C and 2 bar:

$$4HCl(g) + O_2(g) \longrightarrow 2H_2O(g) + 2Cl_2(g)$$
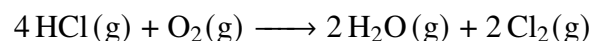
If the system initially contains 5 mol HCl for each mole of oxygen, what is the composition of the system in equilibrium? Assume ideal gases.

Solution

$$n_{\text{HCl}} = 5 \text{ mol} \qquad n_{\text{O}_2} = 1 \text{ mol} \qquad n_0 = 6 \text{ mol}$$
$$T = 773.15 \text{ K} \qquad T_0 = 298.15 \text{ K}$$

We must first determine K thus we use Eq (13.18):

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta G_0^\circ - \Delta H_0^\circ}{RT_0} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\, dT - \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T} \qquad (13.18)$$

Determine ΔG_0° and ΔH_0° from the values of the enthalpies and gibbs energies of formation of the species involved:

$$\Delta H_0^\circ = -75948 \text{ J mol}^{-1}$$
$$\Delta G_0^\circ = -114408 \text{ J mol}^{-1}$$

Next we determine the ΔA, ΔB, ΔC, ΔD of the reaction using the Antoine constants of the species involved:

$$\Delta A = -0.439, \qquad \Delta B = 8 \times 10^{-5}, \qquad \Delta C = 0, \qquad \Delta D = -8.23 \times 10^4$$

Substituting to Eq (13.18):

$$\Delta G^\circ = -12671.71 \text{ J mol}^{-1}$$

Solve for K:

$$K = e^{(-\Delta G/RT)} = 7.1795$$

Solve for the mole fractions with respect to ε:

$$y_{\text{HCl}} = \frac{5 - 4\varepsilon}{6 - \varepsilon}$$
$$y_{\text{O}_2} = \frac{1 - \varepsilon}{6 - \varepsilon}$$
$$y_{\text{H}_2\text{O}} = \frac{2\varepsilon}{6 - \varepsilon}$$
$$y_{\text{Cl}_2} = \frac{2\varepsilon}{6 - \varepsilon}$$

Apply Eq. (13.28):

$$\prod_i (y_i)^{\nu_i} = \left(\frac{P}{P^\circ}\right)^{-\nu} K \qquad (13.28)$$

$$\left(\frac{2\varepsilon}{5 - 4\varepsilon}\right)^4 \left(\frac{6 - \varepsilon}{1 - \varepsilon}\right) = 2K$$
$$\varepsilon = 0.7934$$

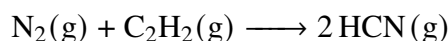$$\boxed{\begin{aligned} y_{\text{HCl}} &= 0.3508 \\ y_{\text{O}_2} &= 0.0397 \\ y_{\text{H}_2\text{O}} &= 0.3048 \\ y_{\text{Cl}_2} &= 0.3048 \end{aligned}}$$

Problem 13.12

The following reaction reaches equilibrium at 650 °C and atmospheric pressure:

$$N_2(g) + C_2H_2(g) \longrightarrow 2\,HCN(g)$$

If the system initially is an equimolar mixture of nitrogen and acetylene, what is the composition of the system at equilibrium? What would be the effect of doubling the pressure? Assume ideal gases.

Solution

Same soution as that of Pb. 13.11

$$n = 2\ \text{mol} \qquad T = 923.15\ \text{K} \qquad \Delta H_0^\circ = 42720\ \text{J mol}^{-1} \qquad \Delta G_0^\circ = 39430\ \text{J mol}^{-1}$$

$$\Delta A = 0.06 \qquad \Delta B = 0.1730 \times 10^{-3} \qquad \Delta C = 0 \qquad \Delta D = -0.191 \times 10^{-5}$$

$$\Delta G_0 = 32421.6383\ \text{J mol}^{-1}$$
$$K = 0.014639$$
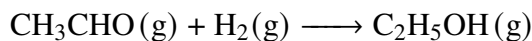$$K = \left(\frac{2\varepsilon}{1-\varepsilon}\right)^2$$
$$\varepsilon = 0.057045$$

$$
\begin{array}{l}
y_{N_2} = 0.471477 \\
y_{C_2H_2} = 0.471477 \\
y_{HCN} = 0.057045
\end{array}
$$

Doubling the pressure does not affect the equilibrium concentration since $v = 0$ then the pressure factor in Eq. (13.28) reduces to 1.

Problem 13.13

The following reaction reaches equilibrium at 350 °C and 3 bar:

$$CH_3CHO(g) + H_2(g) \longrightarrow C_2H_5OH(g)$$

If the system initially contains 1.5 mol H_2 for each mole of acetaldehyde, what is the composition of the system at equilibrium? What would be the effect of reducing the pressure to 1 bar? Assume ideal gases.

$$n_{H_2} = 1.5 \qquad n_{CH_3CHO} = 1 \text{ mol} \qquad n = 2.5 \text{ mol}$$

$$\Delta A = -1.4240 \qquad \Delta B = 1.6010 \times 10^{-3}$$

$$\Delta C = 0.1560 \times 10^{-6} \qquad \Delta D = -0.0830 \times 10^5$$

$$\Delta H_0^\circ = -68910 \text{ J mol}^{-1}$$

$$\Delta G_0^\circ = -39630 \text{ J mol}^{-1}$$

$$K = 3.706095$$

$$\varepsilon = 0.818398$$

$$y_{CH_3CHO} = \frac{1 - \varepsilon}{2.5 - \varepsilon} \qquad y_{H_2} = \frac{1.5 - \varepsilon}{2.5 - \varepsilon} \qquad = y_{CH_3CH_2OH} = \frac{\varepsilon}{2.5 - \varepsilon}$$

$$y_{CH_3CHO} = 0.1080$$
$$y_{H_2} = 0.4053$$
$$y_{CH_3CH_2OH} = 0.4867$$

At 1 bar,

$$\varepsilon = 0.632557$$

$$y_{CH_3CHO} = 0.1968$$
$$y_{H_2} = 0.4645$$
$$y_{CH_3CH_2OH} = 0.3387$$

Problem 13.14

The following reaction reaches equilibrium at 650 °C and atmospheric pressure:

$$C_6H_5CH{=}CH_2(g) + H_2(g) \longrightarrow C_6H_5{-}C_2H_5(g)$$
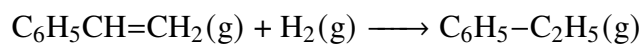
   If the system initially contains 1.5 mol H_2 for each mole of styrene, what is the position of the system at equilibrium? Assume ideal gases.

$$\Delta G^\circ = 2397.343 \text{ J mol}^{-1}$$
$$K = 1.366615$$
$$y_{C_6H_5=CH_2} = \frac{1 - \varepsilon}{2.5 - \varepsilon}$$
$$y_{H_2} = \frac{1.5 - \varepsilon}{2.5 - \varepsilon}$$
$$y_{C_6H_5-C_2H_5} = \frac{\varepsilon}{2.5 - \varepsilon}$$
$$\varepsilon = 0.41554$$

$$\boxed{\begin{array}{c} y_{C_6H_5CH=CH_2} = 0.28039 \\ y_{H_2} = 0.52026 \\ y_{C_6H_5-C_2H_5} = 0.19935 \end{array}}$$

Chapter 14

Problem 14.3

A system formed of methane(1) and a light oil(2) at 200 K and 30 bar consists of a vapor phase containing 95 mol − % methane and a liquid phase containing oil and dissolved methane. The fugacity of the methane is given by Henry's law, and at the temperature of interest Henry's constant is $\mathcal{H}_1 = 200$ bar. Stating any assumptions, estimate the equilibrium mole fraction of methane in the liquid phase. The second virial coefficient of pure methane at 200 K is -105 cm^3 mol^{-1}.

Solution

Given:

$$T = 200 \text{ K} \qquad P = 30 \text{ bar}$$
$$y_1 = 0.95 \text{ mol} \qquad \mathcal{H}_1 = 200 \text{ bar}$$
$$B = -105 \text{ cm}^3 \text{ mol}^{-1}$$

Equations:

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$
$$\hat{\phi}_i = \exp \frac{BP}{RT}$$
$$\hat{f}_i = x_i \mathcal{H}$$

Answer:

$$\boxed{x_1 = 0.1179}$$

Problem 14.46

At 25 °C, the solubility of *n*-hexane in water is 2 ppm (molar basis), and the solubility of water in *n*-hexane is 520 ppm. Estimate the activity coefficients for the two species in the two phases.

Solution

Given:

$$x_1^\alpha = 2 \text{ ppm}$$
$$x_2^\beta = 520 \text{ ppm}$$

Equations:

$$\gamma_1^\alpha = \frac{x_1^\beta}{x_1^\alpha}$$
$$\gamma_2^\beta = \frac{x_2^\alpha}{x_2^\beta}$$

Answers:

$$\boxed{\begin{array}{c} \gamma_1^\alpha = 499740 \\ \gamma_2^\beta = 1923.073 \end{array}}$$