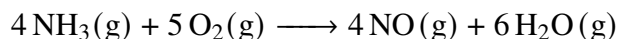


Chapter 13

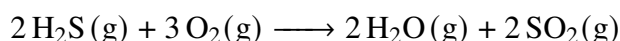
Problem 13.1

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

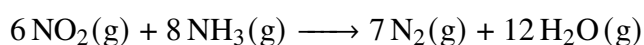
- (a) A system containing 2 mol NH_3 and 5 mol O_2 and undergoing the reaction:



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



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



Solution

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

$$y_i = \frac{n_{io} + v_i \varepsilon}{n_0 + v \varepsilon} \quad (13.5)$$

(a)

$$\begin{aligned} y_{\text{NH}_3} &= \frac{2 - 4\varepsilon}{7 + \varepsilon} \\ y_{\text{O}_2} &= \frac{5 - 5\varepsilon}{7 + \varepsilon} \end{aligned}$$

(b)

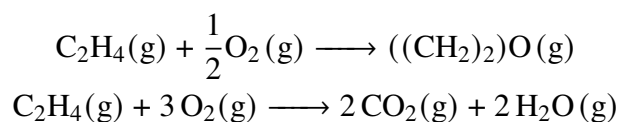
$$\begin{aligned} y_{\text{H}_2\text{S}} &= \frac{3 - 2\varepsilon}{8 - \varepsilon} \\ y_{\text{O}_2} &= \frac{5 - 3\varepsilon}{8 - \varepsilon} \end{aligned}$$

(c)

$$\begin{aligned} y_{\text{NO}_2} &= \frac{3 - 6\varepsilon}{8 + 5\varepsilon} \\ y_{\text{NH}_3} &= \frac{4 - 8\varepsilon}{8 + 5\varepsilon} \\ y_{\text{N}_2} &= \frac{1 + 7\varepsilon}{8 + 5\varepsilon} \end{aligned}$$

Problem 13.2

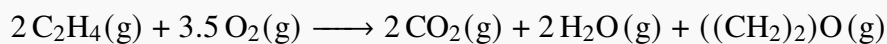
A system initially containing 2 mol C_2H_4 and 3 mol O_2 undergoes the reactions:



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.

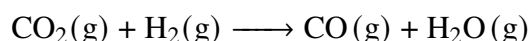
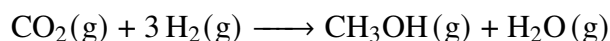


$$y_{\text{C}_2\text{H}_4} = \frac{2 - 2\varepsilon}{5}$$

$$y_{\text{O}_2} = \frac{3 - 3.5\varepsilon}{5}$$

Problem 13.3

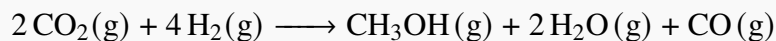
A system formed initially of 2 mol CO_2 , 5 mol H_2 , and 1 mol CO undergoes the reactions:



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.



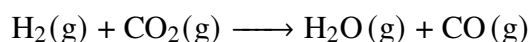
$$y_{\text{CO}_2} = \frac{2 - 2\varepsilon}{8 - 2\varepsilon}$$

$$y_{\text{H}_2} = \frac{5 - 4\varepsilon}{8 - 2\varepsilon}$$

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

Problem 13.4

Consider the water-gas-shift reaction:



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, $G_i = \Delta G_{f_i}^\circ$, for each species, and then:

$$G = \sum_i y_i \Delta G_{f_i}^\circ + RT \sum_i y_i \ln y_i \quad (\text{A})$$

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:

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

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

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

Once the y_i are eliminated in favor of ε , Eq. (A) relates G to ε . Data for $\Delta G_{f_i}^\circ$ for the compounds of interest are given 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 :

- Determine the equilibrium value of ε by application of Eq. (B).
- Plot G vs. ε , indicating the location of the equilibrium value of ε determined in (a).

Solution

- Solving for ε :

$$y_{\text{H}_2} = y_{\text{CO}_2} = \frac{1 - \varepsilon}{2}$$

$$y_{\text{H}_2\text{O}} = y_{\text{CO}} = \frac{\varepsilon}{2}$$

From Eq. (A)—the values of $\Delta G_{f_i}^\circ$ 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):

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

- See Figure 1

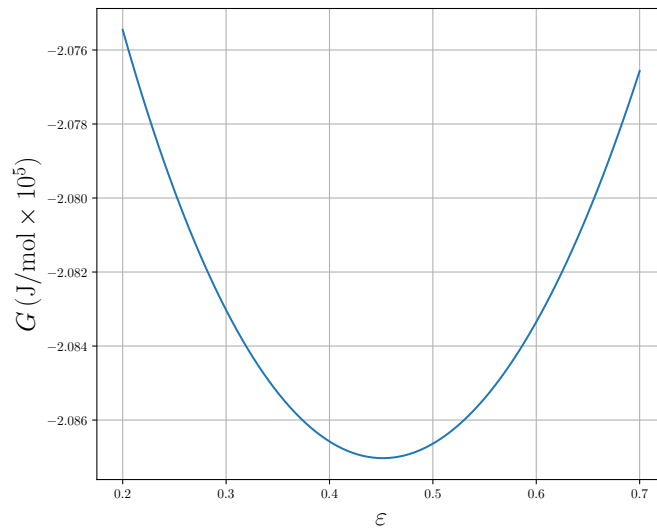


Figure 1: The graph of G with respect to ε for the system described in 13.4

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) $\varepsilon = 0.456$
- (b) $\varepsilon = 0.460$
- (c) $\varepsilon = 0.463$

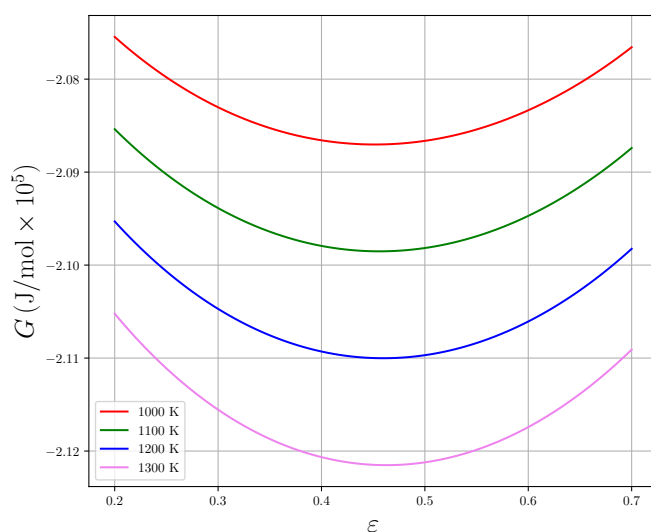


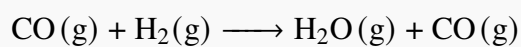
Figure 2: The graph of G with respect to ε for the systems described in 13.5

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



$$y_{\text{H}_2} = y_{\text{CO}_2} = \frac{1 - \varepsilon}{2}$$

$$y_{\text{CO}_2} = y_{\text{H}_2\text{O}} = \frac{\varepsilon}{2}$$

$$K = \frac{y_{\text{H}_2\text{O}} y_{\text{CO}}}{y_{\text{H}_2} y_{\text{CO}}} = \left(\frac{\varepsilon}{1 - \varepsilon} \right)^2$$

$$K = \exp \left(\frac{-\Delta G}{RT} \right)$$

$$\varepsilon = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

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

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.

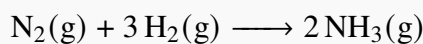
Solution

Write ΔG_r° in terms of K and T :

$$K = e^{-\Delta G_r^\circ/(RT)}$$

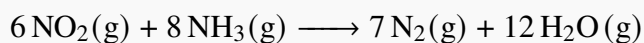
$$\Delta G_r^\circ = RT \ln \left(\frac{1}{K} \right)$$

(a)



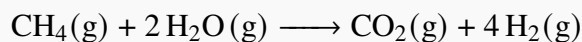
$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{N}_2} y_{\text{H}_2}^2}{y_{\text{NH}_3}^2} \right)$$

(f)



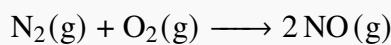
$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{NO}_2}^6 y_{\text{NH}_3}^8}{y_{\text{N}_2}^7 y_{\text{H}_2\text{O}}^{12}} \right)$$

(i)



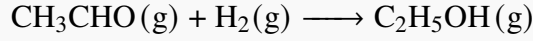
$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{CH}_4} y_{\text{H}_2\text{O}}^2}{y_{\text{CO}_2} y_{\text{H}_2}^4} \right)$$

(n)



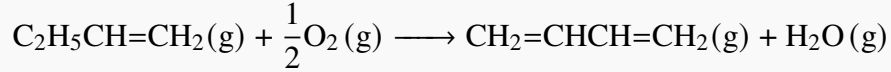
$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{N}_2} y_{\text{O}_2}}{y_{\text{NO}}^2} \right)$$

(r)



$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{CH}_3\text{CHO}} y_{\text{H}_2}}{y_{\text{C}_2\text{H}_5\text{OH}}} \right)$$

(t)



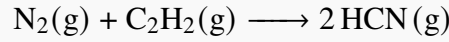
$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{C}_2\text{H}_5\text{CH}=\text{CH}_2} y_{\text{O}_2}^{1/2}}{y_{\text{CH}_2=\text{CHCH}=\text{CH}_2} y_{\text{H}_2\text{O}}} \right)$$

(u)



$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{C}_4\text{H}_{10}}}{y_{\text{CH}_2=\text{CHCH}=\text{CH}_2} y_{\text{H}_2}^2} \right)$$

(x)



$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{N}_2} y_{\text{C}_2\text{H}_2}}{y_{\text{HCN}}^2} \right)$$

(y)



$$\Delta G_r^\circ = RT \ln \left(\frac{y_{\text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_5}}{y_{\text{C}_6\text{H}_5\text{CH}=\text{CH}_2} y_{\text{H}_2}} \right)$$

Problem 13.8

For ideal gases, exact mathematical expressions can be developed for the effect of T and P on ε_e . For conciseness, let $\prod (y_i)^{\nu_i} = K_y$. Then:

$$\left(\frac{\partial \varepsilon_e}{\partial T} \right)_P = \left(\frac{\partial K_y}{\partial T} \right)_P \frac{d\varepsilon_e}{dK_y} \quad \text{and} \quad \left(\frac{\partial \varepsilon_e}{\partial P} \right)_T = \left(\frac{\partial K_y}{\partial P} \right)_T \frac{d\varepsilon_e}{dK_y}$$

Use Eqs. (13.28) and (13.14), to show that:

$$(a) \quad \left(\frac{\partial \varepsilon_e}{\partial T} \right)_P = \frac{K_y}{RT^2} \frac{d\varepsilon_e}{dK_y} \Delta H^\circ$$

$$(b) \left(\frac{\partial \varepsilon_e}{\partial P} \right)_T = - \frac{K_y}{P} \frac{d\varepsilon_e}{dK_y}(\bar{v})$$

- (c) (c) $d\varepsilon_e/dK_y$ is always positive. (Note: It is equally valid and perhaps easier to show that the reciprocal is positive.)