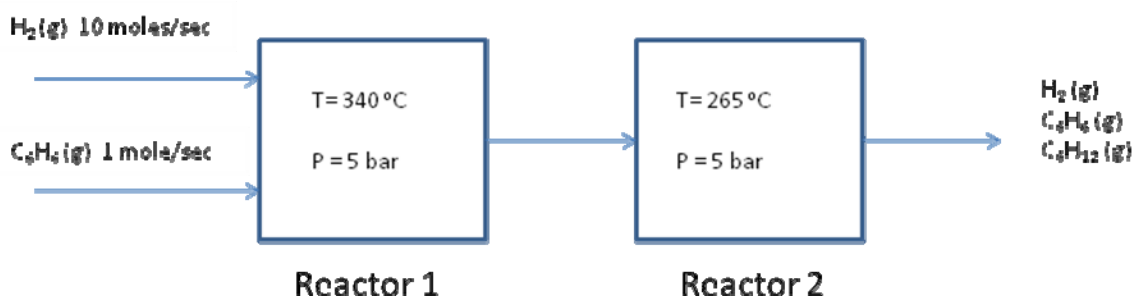


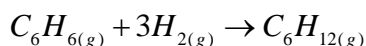
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9.7 Consider the industrial production of cyclohexane,  $C_6H_{12}$ , by the gas-phase hydrogenation of benzene,  $C_6H_6$ . Assume that this process is carried out by two reactors in series as shown below. The first reactor is at  $340^\circ\text{C}$  and 5 bar, while the second reactor is at  $265^\circ\text{C}$  and 5 bar. The feed ratio of hydrogen gas to benzene is 10:1; there is no cyclohexane in the feed. All species are in the gas phase. You may assume ideal gas behavior and that  $\Delta h_{\text{rxn}}^0$  does not change with temperature.



- What is the equilibrium composition at the exit of the second reactor?
- What is the purpose of the first reactor; that is, why do we use two reactors instead of just one?
- Would we get more product if we used a pressure of 1 bar instead of 5 bar? Explain.
- Would you recommend diluting the feed with an inert to increase the yield of  $C_6H_{12}$ ? Explain.

a. We begin by writing the balanced reaction:



To calculate the equilibrium composition leaving the first reactor, we need to follow this path: Calculate  $\Delta g_{\text{rxn}}$ , then  $K$ , then  $\xi$ .

Calculate  $\Delta g_{\text{rxn}}$  first at 298 K.

$$\begin{aligned}\Delta g_{\text{rxn}}^{298} &= \sum_{i=1}^C \nu_i (\Delta g_{f,298}^o)_i \\ &= (1)(\Delta g_{f,C_6H_{12},298}^o) + (-3)(\Delta g_{f,H_2,298}^o) + (-1)(\Delta g_{f,C_6H_6,298}^o) \\ \Delta g_f^o &= 0 \text{ for } H_2 \text{ because it is in its elemental form} \\ &= 31.78 \frac{\text{kJ}}{\text{mol}} - (3 \cdot 0 + 129.75 \frac{\text{kJ}}{\text{mol}}) \\ &= -97.97 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

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Now we can calculate  $K_{298}$

$$\begin{aligned} K_{298} &= \exp\left(\frac{-\Delta g_{rxn,298}}{RT}\right) \\ &= \exp\left(\frac{97.97 \times 10^3 \text{ J/mol}}{8.314 \text{ J/(mol K)} * 298 \text{ K}}\right) \\ &= 1.49 \times 10^{17} \end{aligned}$$

Since reactor 1 operates at a temperature other than 298 K, we must correct the equilibrium constant for the difference in temperature.  $K$  is a function of the heat of reaction, so let's calculate  $\Delta h_{rxn,298}$ .

$$\begin{aligned} \Delta h_{rxn}^{298} &= \sum_{i=1}^C \nu_i (\Delta h_{f,298}^o)_i \\ &= (1)(\Delta h_{f,C_6H_{12},298}^o) + (-3)(\Delta h_{f,H_2,298}^o) + (-1)(\Delta h_{f,C_6H_6,298}^o) \\ \Delta h_f^o &= 0 \text{ for } H_2 \text{ because it is in its elemental form} \\ &= -123.22 \frac{\text{kJ}}{\text{mol}} - (3 * 0 + 82.98 \frac{\text{kJ}}{\text{mol}}) \\ &= -206.2 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

The problem says we may assume  $\Delta h_{rxn}$  is a constant and not a function of temperature. Using this assumption,  $K$  depends only on  $T$ ,  $K_{298}$ , and  $\Delta h_{rxn,298}$ :

$$\begin{aligned} \ln\left(\frac{K_{613K}}{K_{298K}}\right) &= -\frac{\Delta h_{rxn}^o}{R} \left(\frac{1}{613K} - \frac{1}{298K}\right) \\ \ln\left(\frac{K_{613K}}{1.49 * 10^{17}}\right) &= -\frac{-206.2 * 10^3 \text{ J/mol}}{8.314 \text{ J/(mol K)}} \left(\frac{1}{613K} - \frac{1}{298K}\right) \\ K_{613K} &= 0.0398 \end{aligned}$$

Since the reaction occurs in the gas phase and assuming all species behave ideally,

$$\begin{aligned} K &= \prod (y_i)^{\nu_i} P^{\nu} \\ &= \frac{y_{C_6H_{12}}}{y_{C_6H_6} (y_{H_2})^3} P^{-3} \\ \text{where } \nu &= \sum_i \nu_i = -3 \end{aligned}$$

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The moles of each species at equilibrium can be expressed in terms of extent of reaction,  $\xi$ .

$$n_{C_6H_6} = n_{C_6H_6}^o + \nu_{C_6H_6} \xi = 1 - \xi$$

$$n_{H_2} = n_{H_2}^o + \nu_{H_2} \xi = 10 - 3\xi$$

$$n_{C_6H_{12}} = n_{C_6H_{12}}^o + \nu_{C_6H_{12}} \xi = \xi$$

$$n = \sum_{i=1}^C n_i = 11 - 3\xi$$

$$y_i = \frac{n_i}{n}$$

$$y_{C_6H_6} = \frac{1-\xi}{11-3\xi}, \quad y_{C_6H_{12}} = \frac{\xi}{11-3\xi}, \quad y_{H_2} = \frac{10-3\xi}{11-3\xi}$$

Substituting these expressions into the equation for  $K_{613}$ :

$$K = \frac{y_{C_6H_{12}}}{y_{C_6H_6} (y_{H_2})^3} P^{-3}$$

$$0.0398 = \frac{\left(\frac{\xi}{11-3\xi}\right)}{\left(\frac{10-3\xi}{11-3\xi}\right)^3 \left(\frac{1-\xi}{11-3\xi}\right)} (5\text{bar})^{-3}$$

Solving for  $\xi$ ,

$$\xi = 0.78$$

The number of moles of  $C_6H_6$ ,  $H_2$ , and  $C_6H_{12}$  leaving the first reactor are thus

$$n_{C_6H_6} = 1 - 0.775 = 0.225 \text{ mol } C_6H_6$$

$$n_{H_2} = 10 - 3(0.775) = 7.675 \text{ mol } H_2$$

$$n_{C_6H_{12}} = 0.775 \text{ mol } C_6H_{12}$$

We now use these amounts as the feed to the second reactor. Since Reactor 2 occurs at a different temperature than Reactor 1, we have to adjust our K.

$$\ln\left(\frac{K_{538K}}{K_{298K}}\right) = -\frac{\Delta h_{rxn}^o}{R} \left(\frac{1}{538K} - \frac{1}{298K}\right)$$

$$\ln\left(\frac{K_{538K}}{1.49 \times 10^{17}}\right) = -\frac{-206.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/(mol K)}} \left(\frac{1}{538K} - \frac{1}{298K}\right)$$

$$K_{538K} = 11.196$$

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Using the compositions leaving the first reactor as our initial amounts of species  $i$ , we can calculate the extent of reaction in the 2<sup>nd</sup> reactor:

$$K = \frac{y_{C_6H_{12}}}{y_{C_6H_6} (y_{H_2})^3} P^{-3}$$

$$11.2 = \frac{\left( \frac{0.775 + \xi}{8.675 - 3\xi} \right)}{\left( \frac{7.675 - 3\xi}{8.675 - 3\xi} \right) \left( \frac{0.225 - \xi}{8.675 - 3\xi} \right)} (5\text{bar})^{-3}$$

$$\xi = 0.224$$

The equilibrium composition leaving the second reactor is then:

$$n_{C_6H_6} = 0.225 - 0.224 = 0.001 \text{ mol } C_6H_6$$

$$n_{H_2} = 7.675 - 3(0.224) = 7.003 \text{ mol } H_2$$

$$n_{C_6H_{12}} = 0.999 \text{ mol } C_6H_{12}$$

b. *What is the purpose of the first reactor; that is, why do we use two reactors instead of just one?*

From Koretsky:

The purpose of the first reactor is to increase the speed of the process. At higher temperatures, more collisions occur with sufficient energy to overcome the activation energy of the reaction. However, as the temperature increases, the conversion decreases. The second reactor increases the conversion.

c. *Would we get more product if we used a pressure of 1 bar instead of 5 bar? Explain.*

From part a., for this reaction, stoichiometry dictates that  $K \propto P^{-3}$ , where  $\sum_i \nu_i = -3$ . If  $P$  decreases,  $K$  increases and more product would be formed.

d. *Would you recommend diluting the feed with an inert to increase the yield of  $C_6H_{12}$ ? Explain.*

The presence of inerts affects the total number of moles in the mixture,  $n$ . From part a.,  $K \propto n^{-3}$ . If inerts are added, the total number of moles in the reaction mixture increases, and  $K$  decreases. Thus, the overall yield of  $C_6H_{12}$  would decrease if inerts are added.