

6.4 THE GIBBS ENERGY OF A REACTION MIXTURE

To this point, the discussion has been limited to systems at a fixed composition. Our focus in the rest of the chapter is in using the Gibbs energy to understand equilibrium in a reaction mixture under constant pressure conditions, which correspond to typical laboratory experiments. Because reactants are consumed and products are generated in chemical reactions, the expressions derived for state functions such as U , H , S , A , and G must be revised to include changes in composition. We focus on G in the following discussion.

For a reaction mixture containing species 1, 2, 3, ..., G is no longer a function of the variables T and P only. Because it depends on the number of moles of each species, G is written in the form $G = G(T, P, n_1, n_2, n_3, \dots)$. The total differential dG is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, \dots} dn_2 + \dots \quad (6.36)$$

Note that if the concentrations do not change, all of the $dn_i = 0$, and Equation (6.36) reduces to $dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$.

Equation (6.36) can be simplified by defining the chemical potential, μ_i , as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} \quad (6.37)$$

It is important to realize that although μ_i is defined mathematically in terms of an infinitesimal change in the amount dn_i of species i , the chemical potential μ_i is the change in the Gibbs energy per mole of substance i added at constant concentration. These two requirements are not contradictory. To keep the concentration constant, one adds a mole of substance i to a huge vat containing many moles of the various species. In this case, the slope of a plot of G versus n_i is the same if the differential $(\partial G / \partial n_i)_{T, P, n_j \neq n_i}$ is formed, where $dn_i \rightarrow 0$, or the ratio $(\Delta G / \Delta n_i)_{T, P, n_j \neq n_i}$ is formed, where Δn_i is 1 mol. Using the notation of Equation (6.37), Equation (6.36) can be written as follows:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \sum_i \mu_i dn_i \quad (6.38)$$

Now imagine integrating Equation (6.38) at constant composition and at constant T and P from an infinitesimal size of the system where $n_i \rightarrow 0$ and therefore $G \rightarrow 0$ to a macroscopic size where the Gibbs energy has the value G . Because T and P are constant, the first two terms in Equation (6.38) do not contribute to the integral. Because the composition is constant, μ_i is constant,

$$\int_0^G dG' = \sum_i \mu_i \int_0^{n_i} dn'_i$$

$$G = \sum_i n_i \mu_i \quad (6.39)$$

Note that because μ_i depends on the number of moles of each species present, it is a function of concentration. If the system consists of a single pure substance A , $G = n_A G_{m,A}$ because G is an extensive quantity. Applying Equation (6.37),

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P, T} = \left(\frac{\partial [n_A G_{m,A}]}{\partial n_A}\right)_{P, T} = G_{m,A}$$

showing that μ_A is an intensive quantity equal to the molar Gibbs energy of A for a pure substance. As seen later, however, this statement is not true for mixtures.

Why is μ_i called the chemical potential of species i ? This can be understood by assuming that the chemical potential for species i has the values μ_i^I in region I, and μ_i^{II} in region II of a given mixture with $\mu_i^I > \mu_i^{II}$. If dn_i moles of species i are transported from region I to region II, at constant T and P , the change in G is given by

$$dG = -\mu_i^I dn_i + \mu_i^{II} dn_i = (\mu_i^{II} - \mu_i^I) dn_i < 0 \quad (6.40)$$

Because $dG < 0$, this process is spontaneous. For a given species, transport will occur spontaneously from a region of high chemical potential to one of low chemical potential. The flow of material will continue until the chemical potential has the same value in all regions of the mixture. Note the analogy between this process and the flow of mass in a gravitational potential or the flow of charge in an electrostatic potential. Therefore, the term *chemical potential* is appropriate.

In this discussion, we have defined a new criterion for equilibrium in a multicomponent mixture: At equilibrium, the chemical potential of each individual species is the same throughout a mixture.

6.5 THE GIBBS ENERGY OF A GAS IN A MIXTURE

In the next three sections, the conditions for equilibrium in a reactive mixture of ideal gases are derived in terms of the μ_i of the chemical constituents. Imagine that we have a reaction vessel in which all reactants are initially confined to separate volumes through barriers that are suddenly removed to let the reaction proceed. Two important processes occur, namely (i) the mixing of reactants and products and (ii) the conversion of reactants to products. In both processes, the partial pressures of individual species and their chemical potentials change. In this section, we describe how the chemical potential of a reactant or product species changes as its concentration in the reaction mixture changes. In the next section, we describe how the chemical potential of a reactant or product species changes through mixing. Using these results, we show in Section 6.7 that the partial pressures of all constituents of the reaction mixture are related by the thermodynamic equilibrium constant, K_p .

Consider first the simple system consisting of two volumes separated by a semipermeable membrane, as shown in Figure 6.2. On the left side, the gas consists solely of pure H_2 . On the right side, H_2 is present as one constituent of a mixture. The membrane allows only H_2 to pass in both directions.

Once equilibrium has been reached with respect to the concentration of H_2 throughout the system, the hydrogen pressure (but not the total pressure) is the same on both sides of the membrane and therefore

$$\mu_{H_2}^{pure} = \mu_{H_2}^{mixture} \quad (6.41)$$

Recall from Section 6.3 that the molar Gibbs energy of a pure ideal gas depends on its pressure as $G(T, P) = G^\circ(T) + nRT \ln(P/P^\circ)$. Therefore, Equation (6.41) can be written in the form

$$\mu_{H_2}^{pure}(T, P_{H_2}) = \mu_{H_2}^{mixture}(T, P_{H_2}) = \mu_{H_2}^\circ(T) + RT \ln \frac{P_{H_2}}{P^\circ} \quad (6.42)$$

The chemical potential of a gas in a mixture depends logarithmically on its partial pressure. Equation (6.42) applies to any mixture, not just to those for which an appropriate semipermeable membrane exists. We, therefore, generalize the discussion by referring to a component of the mixture as A.

The partial pressure of species A in the gas mixture, P_A , can be expressed in terms of x_A , its mole fraction in the mixture, and the total pressure, P :

$$P_A = x_A P \quad (6.43)$$

Using this relationship, Equation (6.42) becomes

$$\begin{aligned} \mu_A^{mixture}(T, P) &= \mu_A^\circ(T) + RT \ln \frac{P}{P^\circ} + RT \ln x_A \\ &= \left(\mu_A^\circ(T) + RT \ln \frac{P}{P^\circ} \right) + RT \ln x_A \text{ or} \\ \mu_A^{mixture}(T, P) &= \mu_A^{pure}(T, P) + RT \ln x_A \end{aligned} \quad (6.44)$$

Because $\ln x_A < 0$, we find that the chemical potential of a gas in a mixture is less than that of the pure gas if the total pressure P is the same for the pure sample and the mixture. This is the case because $P_A < P$. Because $\mu_A^{mixture}(T, P) < \mu_A^{pure}(T, P)$, diffusion of H_2 from the left side to the right side of the system in Figure 6.2 will continue until the partial pressures of H_2 on both sides of the membrane are equal. We can conclude from Equation 6.44 that mixing of the two subsystems would be spontaneous if they were not separated by the membrane.

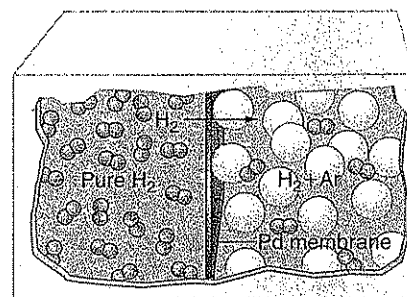


FIGURE 6.2

An isolated system consists of two subsystems. Pure H_2 gas is present on the left of a palladium membrane that is permeable to H_2 , but not to argon. The H_2 is contained in a mixture with Ar in the subsystem to the right of the membrane.

6.6 CALCULATING THE GIBBS ENERGY OF MIXING FOR IDEAL GASES

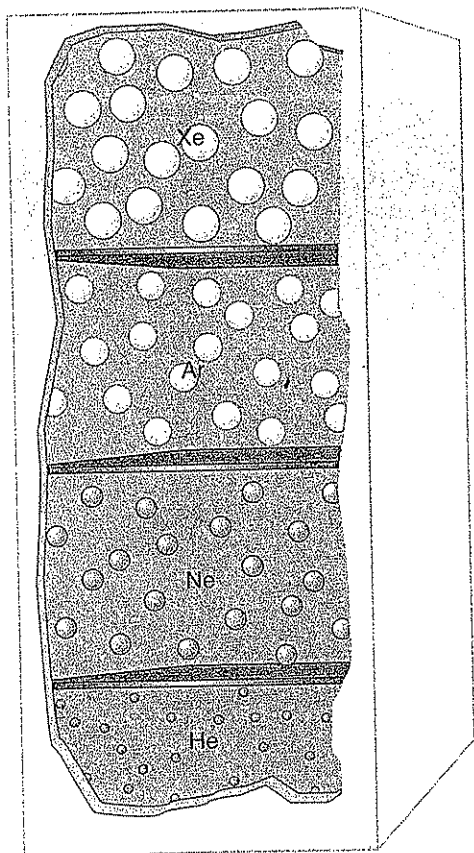


FIGURE 6.3

An isolated system consists of four separate subsystems containing He, Ne, Ar, and Xe, each at a pressure of 1 bar. The barriers separating these subsystems can be removed, leading to mixing.

In the previous section, we derived a relation between the chemical potential of a species in a mixture, the chemical potential of the pure species, and the mole fraction of the species in the mixture. We also demonstrated that the mixing of gases is a spontaneous process, so that ΔG_{mixing} must be negative. We now obtain a quantitative relationship between ΔG_{mixing} and the mole fractions of the individual constituents of the mixture. Consider the system shown in Figure 6.3. The four compartments contain the gases He, Ne, Ar, and Xe at the same temperature and pressure. The volumes of the four compartments differ. To calculate ΔG_{mixing} , we must compare G for the initial state shown in Figure 6.3 and the final state. For the initial state, in which we have four pure separated substances,

$$G_i = G_{\text{He}} + G_{\text{Ne}} + G_{\text{Ar}} + G_{\text{Xe}} = n_{\text{He}}G_{\text{He}}^\circ + n_{\text{Ne}}G_{\text{Ne}}^\circ + n_{\text{Ar}}G_{\text{Ar}}^\circ + n_{\text{Xe}}G_{\text{Xe}}^\circ \quad (6.45)$$

For the final state in which all four components are dispersed in the mixture, from Equation (6.44),

$$G_f = n_{\text{He}}(G_{\text{He}}^\circ + RT \ln x_{\text{He}}) + n_{\text{Ne}}(G_{\text{Ne}}^\circ + RT \ln x_{\text{Ne}}) + n_{\text{Ar}}(G_{\text{Ar}}^\circ + RT \ln x_{\text{Ar}}) + n_{\text{Xe}}(G_{\text{Xe}}^\circ + RT \ln x_{\text{Xe}}) \quad (6.46)$$

The Gibbs energy of mixing is $G_f - G_i$ or

$$\begin{aligned} \Delta G_{\text{mixing}} &= RTn_{\text{He}} \ln x_{\text{He}} + RTn_{\text{Ne}} \ln x_{\text{Ne}} + RTn_{\text{Ar}} \ln x_{\text{Ar}} + RTn_{\text{Xe}} \ln x_{\text{Xe}} \\ &= RT \sum_i n_i \ln x_i = nRT \sum_i x_i \ln x_i \end{aligned} \quad (6.47)$$

Note that because each term in the last expression of Equation (6.47) is negative $\Delta G_{\text{mixing}} < 0$. We again verify that mixing is a spontaneous process.

Equation (6.47) allows us to calculate ΔG_{mixing} for any given set of the mole fractions x_i . It is easiest to graphically visualize the results for a binary mixture of species A and B. To simplify the notation, we set $x_A = x$, so that $x_B = 1 - x$. It follows that

$$\Delta G_{\text{mixing}} = nRT[x \ln x + (1 - x) \ln (1 - x)] \quad (6.48)$$

A plot of ΔG_{mixing} versus x is shown in Figure 6.4 for a binary mixture. Note that ΔG_{mixing} is zero for $x_A = 0$ and $x_A = 1$ because only pure substances are present in these limits. Also, ΔG_{mixing} has a minimum for $x_A = 0.5$, because the maximal decrease in G arises from the mixing when A and B are present in equal amounts.

The entropy of mixing can be calculated from Equation (6.47):

$$\Delta S_{\text{mixing}} = -\left(\frac{\partial \Delta G_{\text{mixing}}}{\partial T}\right)_P = -nR \sum_i x_i \ln x_i \quad (6.49)$$

cause of the increase in entropy! Each of the two components of the mixture expands from its initial volume to the same final volume. Therefore, ΔS_{mixing} arises from the dependence of S on V at constant T . We verify this assertion using the expression derived in Section 5.4 for the change of S with V , and obtain Equation (6.49).

$$\begin{aligned}\Delta S &= R \left(n_A \ln \frac{V_f}{V_{iA}} + n_B \ln \frac{V_f}{V_{iB}} \right) = R \left(n x_A \ln \frac{1}{x_A} + n x_B \ln \frac{1}{x_B} \right) \\ &= -nR(x_A \ln x_A + x_B \ln x_B)\end{aligned}$$

if both components and the mixture are at the same pressure.

EXAMPLE PROBLEM 6.5

Consider the system shown in Figure 6.3. Assume that the separate compartments contain 1.0 mol of He, 3.0 mol of Ne, 2.0 mol of Ar, and 2.5 mol of Xe at 298.15 K. The pressure in each compartment is 1 bar.

- Calculate ΔG_{mixing} .
- Calculate ΔS_{mixing} .

Solution

$$\begin{aligned}\text{a. } \Delta G_{\text{mixing}} &= RTn_{\text{He}} \ln x_{\text{He}} + RTn_{\text{Ne}} \ln x_{\text{Ne}} + RTn_{\text{Ar}} \ln x_{\text{Ar}} + RTn_{\text{Xe}} \ln x_{\text{Xe}} \\ &= RT \sum_i n_i \ln x_i = nRT \sum_i x_i \ln x_i \\ &= 8.5 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \\ &\quad \times \left(\frac{1.0}{8.5} \ln \frac{1.0}{8.5} + \frac{3.0}{8.5} \ln \frac{3.0}{8.5} + \frac{2.0}{8.5} \ln \frac{2.0}{8.5} + \frac{2.5}{8.5} \ln \frac{2.5}{8.5} \right) \\ &= -2.8 \times 10^4 \text{ J} \\ \text{b. } \Delta S_{\text{mixing}} &= -nR \sum_i x_i \ln x_i \\ &= -8.5 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ &\quad \times \left(\frac{1.0}{8.5} \ln \frac{1.0}{8.5} + \frac{3.0}{8.5} \ln \frac{3.0}{8.5} + \frac{2.0}{8.5} \ln \frac{2.0}{8.5} + \frac{2.5}{8.5} \ln \frac{2.5}{8.5} \right) \\ &= 93 \text{ J K}^{-1}\end{aligned}$$

What is the driving force for the mixing of gases? We saw in Section 6.1 that there are two contributions to ΔG , an enthalpic contribution ΔH and an entropic contribution $T\Delta S$. By calculating ΔH_{mixing} from $\Delta H_{\text{mixing}} = \Delta G_{\text{mixing}} + T\Delta S_{\text{mixing}}$ using Equations (6.48) and (6.49), you will see that for the mixing of ideal gases, $\Delta H_{\text{mixing}} = 0$. Because the molecules in an ideal gas do not interact, there is no enthalpy change associated with mixing. We conclude that the mixing of ideal gases is driven entirely by ΔS_{mixing} as shown above.

Although the mixing of gases is always spontaneous, the same is not true of liquids. Liquids can be either miscible or immiscible. How can this observation be explained? For gases or liquids, $\Delta S_{\text{mixing}} > 0$. Therefore, if two liquids are immiscible, $\Delta G_{\text{mixing}} > 0$ because $\Delta H_{\text{mixing}} > 0$ and $\Delta H_{\text{mixing}} > T\Delta S_{\text{mixing}}$. If two liquids mix, it is generally energetically favorable for one species to be surrounded by the other species. In this case, $\Delta H_{\text{mixing}} < T\Delta S_{\text{mixing}}$, and $\Delta G_{\text{mixing}} < 0$.

It is important to understand that the equilibrium condition of Equation (6.60) links the partial pressures of all reactants and products. Imagine that a quantity of species D is added to the system initially at equilibrium. The system will reach a new equilibrium state in which P_A^{eq} , P_B^{eq} , P_C^{eq} , and P_D^{eq} all have new values because the value of $K_P = \left(\frac{P_C^{\text{eq}}}{P^\circ} \right)^\gamma \left(\frac{P_D^{\text{eq}}}{P^\circ} \right)^\delta / \left(\frac{P_A^{\text{eq}}}{P^\circ} \right)^\alpha \left(\frac{P_B^{\text{eq}}}{P^\circ} \right)^\beta$ does not change.

EXAMPLE PROBLEM 6.9

- Using data from Table 4.1 (see Appendix B, Data Tables), calculate K_P at 298.15 K for the reaction $\text{CO}(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$.
- Based on the value that you obtained for part (a), do you expect the mixture to consist mainly of $\text{CO}_2(g)$ and $\text{H}_2(g)$ or mainly of $\text{CO}(g) + \text{H}_2\text{O}(l)$ at equilibrium?

Solution

$$\begin{aligned}\text{a. } \ln K_P &= -\frac{1}{RT} \Delta G_R^\circ \\ &= -\frac{1}{RT} \left(\Delta G_f^\circ(\text{CO}_2, g) + \Delta G_f^\circ(\text{H}_2, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) \right. \\ &\quad \left. - \Delta G_f^\circ(\text{CO}, g) \right) \\ &= -\frac{1}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \\ &\quad \times \left(-394.4 \times 10^3 \text{ J mol}^{-1} + 0 + 237.1 \right. \\ &\quad \left. \times 10^3 \text{ J mol}^{-1} + 137.2 \times 10^3 \text{ J mol}^{-1} \right) \\ &= 8.1087 \\ K_P &= 3.32 \times 10^3\end{aligned}$$

- Because $K_P \gg 1$, the mixture will consist mainly of the products $\text{CO}_2(g) + \text{H}_2(g)$ at equilibrium.

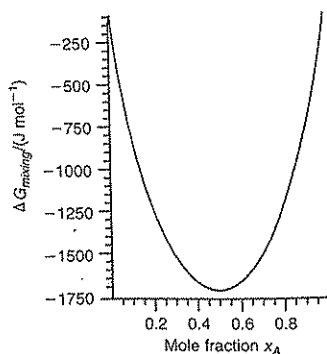


FIGURE 6.4

The Gibbs energy of mixing of the ideal gases A and B as a function of x_A , with $n_A + n_B = 1$ and $T = 298.15 \text{ K}$.

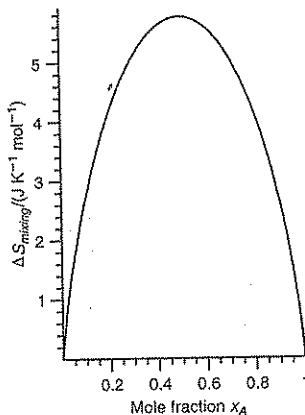


FIGURE 6.5

The entropy of mixing of the ideal gases A and B is shown as a function of the mole fraction of component A at 298.15 K, with $n_A + n_B = 1$.

6.8 INTRODUCING THE EQUILIBRIUM CONSTANT FOR A MIXTURE OF IDEAL GASES

In a reaction mixture with a total pressure of 1 bar, the partial pressure of each species, P_i , is less than the standard state pressure of 1 bar. In this section, we introduce the pressure dependence of μ_i in order to calculate ΔG_R for such reaction mixtures. Consider the following reaction that takes place between ideal gas species A, B, C, and D:



Because all four species are present in the reaction mixture, the reaction Gibbs energy for the arbitrary set of partial pressures P_A , P_B , P_C , and P_D , is given by

$$\begin{aligned} \Delta G_R = \sum_i v_i \Delta G_{f,i} &= \gamma \mu_C^\circ + \gamma RT \ln \frac{P_C}{P^\circ} + \delta \mu_D^\circ + \delta RT \ln \frac{P_D}{P^\circ} \\ &\quad - \alpha \mu_A^\circ - \alpha RT \ln \frac{P_A}{P^\circ} - \beta \mu_B^\circ - \beta RT \ln \frac{P_B}{P^\circ} \end{aligned} \quad (6.55)$$

The terms in the previous equation can be separated into those at the standard condition of $P^\circ = 1$ bar and the remaining terms:

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + \gamma RT \ln \frac{P_C}{P^\circ} + \delta RT \ln \frac{P_D}{P^\circ} - \alpha RT \ln \frac{P_A}{P^\circ} - \beta RT \ln \frac{P_B}{P^\circ} \\ &= \Delta G_R^\circ + RT \ln \frac{\left(\frac{P_C}{P^\circ}\right)^\gamma \left(\frac{P_D}{P^\circ}\right)^\delta}{\left(\frac{P_A}{P^\circ}\right)^\alpha \left(\frac{P_B}{P^\circ}\right)^\beta} \end{aligned} \quad (6.56)$$

where

$$\Delta G_R^\circ = \gamma \mu_C^\circ(T) + \delta \mu_D^\circ(T) - \alpha \mu_A^\circ(T) - \beta \mu_B^\circ(T) = \sum_i v_i \Delta G_{f,i}^\circ \quad (6.57)$$

Recall from Example Problem 6.6 that standard Gibbs energies of formation rather than chemical potentials are used to calculate ΔG_R° .

The combination of the partial pressures of reactants and products is called the **reaction quotient of pressures**, which is abbreviated Q_P and defined as follows:

$$Q_P = \frac{\left(\frac{P_C}{P^\circ}\right)^\gamma \left(\frac{P_D}{P^\circ}\right)^\delta}{\left(\frac{P_A}{P^\circ}\right)^\alpha \left(\frac{P_B}{P^\circ}\right)^\beta} \quad (6.58)$$

With these definitions of ΔG_R° and Q_P , Equation (6.55) becomes

$$\Delta G_R = \Delta G_R^\circ + RT \ln Q_P \quad (6.59)$$

Note this important result that ΔG_R can be separated into two terms, only one of which depends on the partial pressures of reactants and products.

We next show how Equation (6.59) can be used to predict the direction of spontaneous change for a given set of partial pressures of the reactants and products. If the partial pressures of the products C and D are large, and those of the reactants A and B are small compared to their values at equilibrium, Q_P will be large. As a result, $RT \ln Q_P$ will be large and positive, and $\Delta G_R = \Delta G_R^\circ + RT \ln Q_P > 0$. In this case, the reaction as written in Equation (6.54) from left to right is not spontaneous, but the reverse of the reaction is spontaneous. Next, consider the opposite extreme. If the partial pressures of the reactants A and B are large, and those of the products C and D are small compared to their values at equilibrium, Q_P will be small. As a result, $RT \ln Q_P$ will be large and negative. In this case, $\Delta G_R = \Delta G_R^\circ + RT \ln Q_P < 0$ and the reaction will be spontaneous as written from left to right, as some of the reactants combine to form products.

EXAMPLE PROBLEM 6.8

$\text{NO}_2(g)$ and $\text{N}_2\text{O}_4(g)$ are in a reaction vessel with partial pressures of 0.350 and 0.650 bar, respectively, at 298 K. Is this system at equilibrium? If not, must the system move toward reactants or products to reach equilibrium?

Solution

The reaction of interest is $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$. We calculate ΔG_R using $\Delta G_R = \Delta G_R^\circ + RT \ln Q_P$:

$$\begin{aligned} \Delta G_R &= 99.8 \text{ kJ mol}^{-1} - 2 \times 51.3 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{K}^{-1} \\ &\quad \times 298 \text{ K} \ln \frac{0.650 \text{ bar/1 bar}}{(0.350 \text{ bar/1 bar})^2} \\ &= -2.80 \times 10^3 \text{ J mol}^{-1} + 4.13 \times 10^3 \text{ J mol}^{-1} \\ &= 1.33 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

Because $\Delta G_R \neq 0$, the system is not at equilibrium. Because $\Delta G_R > 0$, the system moves toward reactants.

Whereas the two cases that we have considered lead to a change in the partial pressures of the reactants and products, the most interesting case is equilibrium for which $\Delta G_R = 0$. At equilibrium, $\Delta G_R^\circ = -RT \ln Q_P$. We denote this special system configuration by adding a superscript *eq* to each partial pressure, and renaming Q_P as K_P . The quantity K_P is called the **thermodynamic equilibrium constant**:

$$0 = \Delta G_R^\circ + RT \ln \frac{\left(\frac{P_C^{eq}}{P^\circ}\right)^\gamma \left(\frac{P_D^{eq}}{P^\circ}\right)^\delta}{\left(\frac{P_A^{eq}}{P^\circ}\right)^\alpha \left(\frac{P_B^{eq}}{P^\circ}\right)^\beta} \text{ or, equivalently, } \Delta G_R^\circ = -RT \ln K_P$$

or

$$\ln K_P = -\frac{\Delta G_R^\circ}{RT} \quad (6.60)$$

Because ΔG_R° is a function of T only, K_P is also a function of T only. The thermodynamic equilibrium constant K_P does not depend on the pressure. Note also that K_P is a dimensionless number.