

Chemical Equilibrium

One of the most fundamental applications of thermodynamics is to chemical reactions at equilibrium. The underlying fundamental idea that we describe here is that $\Delta G = 0$ for a system in equilibrium (at constant temperature and pressure), and the sign of ΔG determines whether or not a given process or chemical reaction will occur spontaneously at constant T and P.

Consider a general gas phase chemical reaction



We define a quantity ξ , called the extent of reaction such that the numbers of moles of reactants and products are given by

$$n_A = n_{A0} - v_A \xi$$

$$n_B = n_{B0} - v_B \xi$$

$$n_Y = n_{Y0} + v_Y \xi$$

$$n_Z = n_{Z0} + v_Z \xi$$

where n_{j0} is the initial number of moles for each species.

According to the equations above ξ must have units of moles. As the reaction proceeds from reactants to products, ξ varies from 0 to some maximum value dictated by the stoichiometry of the reaction. Differentiation of the equations gives that rate of change of the number of moles.

Reactants

$$dn_A = -v_A d\xi$$

$$dn_B = -v_B d\xi$$

Products

$$dn_Y = v_Y d\xi$$

$$dn_Z = v_Z d\xi$$

The negative signs indicate that the reactants are disappearing and the positive signs indicate that the products are being formed as the reaction progresses from reactants to products.

Now consider a system containing reactions and products

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

At constant T and P we have

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

or using the above expression

$$dG = -\mu_A \nu_A d\xi - \mu_B \nu_B d\xi + \mu_Y \nu_Y d\xi + \mu_Z \nu_Z d\xi$$

or

$$dG = (\mu_Y \nu_Y + \mu_Z \nu_Z - \mu_A \nu_A - \mu_B \nu_B) d\xi$$

or

$$(\partial G / \partial \xi) = (\mu_Y \nu_Y + \mu_Z \nu_Z - \mu_A \nu_A - \mu_B \nu_B)$$

We define the standard free energy of a reaction as $(\partial G / \partial \xi)$. In other words, $(\partial G / \partial \xi) = \Delta_r G$. As we have seen the units of $\Delta_r G$ are J/mole. The quantity $\Delta_r G$ has meaning only if the balanced chemical equation is specified.

If all of the gases in the reaction are ideal then

$$\mu_j(T, P) = \mu_j^\circ(T) + RT(\ln P_j / P^\circ)$$

and substituting this expression into the above equation we find

$$\begin{aligned} \Delta_r G &= \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T) \\ &+ RT \left(\nu_Y \ln \frac{P_Y}{P_Y^\circ} + \nu_Z \ln \frac{P_Z}{P_Z^\circ} - \nu_A \ln \frac{P_A}{P_A^\circ} - \nu_B \ln \frac{P_B}{P_B^\circ} \right) \end{aligned}$$

or

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where

$$\Delta_r G^\circ = \mu_Y^\circ \nu_Y + \mu_Z^\circ \nu_Z - \mu_A^\circ \nu_A - \mu_B^\circ \nu_B$$

and

$$Q = \frac{(P_Y / P_Y^\circ)^{\nu_Y} (P_Z / P_Z^\circ)^{\nu_Z}}{(P_A / P_A^\circ)^{\nu_A} (P_B / P_B^\circ)^{\nu_B}}$$

The quantity $\Delta_r G^\circ$ is the standard Gibbs energy for the reaction between unmixed reactants in their standard states at temperature T and a pressure of one bar to form unmixed products in their standard states at the same T and P. The quantity Q is called the reaction quotient. Its magnitude is dependent on the quantity of reactant and product at any given point during the chemical reaction. The pressures in Q are all referenced to $P^\circ = 1$ bar which

is the standard state. Since $P^\circ = 1$ bar it need not be written explicitly and is often implied in the expression for Q. Thus, Q may have the form

$$Q = \frac{(P_Y)^{\nu_Y}(P_Z)^{\nu_Z}}{(P_A)^{\nu_A}(P_B)^{\nu_B}}$$

where P_j is the partial pressure of the jth component.

When the system is in equilibrium, the Gibbs energy is a minimum

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G = 0$$

In this case, find that the reaction quotient has a special value known as the equilibrium constant.

$$\Delta_r G^\circ = -RT \ln \left(\frac{(P_Y)^{\nu_Y}(P_Z)^{\nu_Z}}{(P_A)^{\nu_A}(P_B)^{\nu_B}} \right) = -RT \ln K(T)$$

We have identified the set of partial pressures consistent with equilibrium with a constant $K(T)$ known as the equilibrium constant.

$$K(T) = \left(\frac{(P_Y)^{\nu_Y}(P_Z)^{\nu_Z}}{(P_A)^{\nu_A}(P_B)^{\nu_B}} \right)_{eq}$$

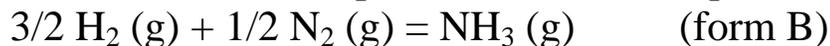
Example: Determine the equilibrium constant expression for the reaction that is represented by the equation



.The stoichiometric coefficients appear as exponents in the expression for the equilibrium constant.

$$K(T) = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3(P_{\text{N}_2})}$$

Note that if we were to express the chemical equation as



the Gibbs free energy would be exactly half as large as form A of the chemical equation above. The equilibrium constant in this case is

$$K(T) = \frac{(P_{NH_3})}{(P_{H_2})^{3/2}(P_{N_2})^{1/2}}$$

The equilibrium constant is a function of temperature only. We may start with any given initial pressures, but the equilibrium constant tells us that the ratio of the pressures products to that of reactions (raised to their respective stoichiometric coefficients) is fixed at equilibrium. When the total pressure appears in the equilibrium constant it can only change the relative proportion of the products and reactants.

Consider, for example, the reaction



The equilibrium constant expression for this reaction is

$$K(T) = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})}$$

Suppose that we initially have 1 mole of PCl_5 . At equilibrium, x moles will have reacted so there will $1 - \xi$ moles of PCl_5 . There will be x moles each of PCl_3 and Cl_2 . Thus, the total number of moles will be $1 - \xi + \xi + \xi = 1 + \xi$. Using Dalton's law we can express the partial pressure of each of the components at equilibrium

$$P_{PCl_3} = P_{Cl_2} = \frac{\xi P}{1 + \xi}$$

$$P_{PCl_5} = \frac{(1 - \xi)P}{1 + \xi}$$

where P is the total pressure. The x represented here are those observed at equilibrium. Substituting these expression into the equilibrium constant we find

$$K(T) = \frac{\xi^2 P}{1 - \xi^2}$$

Although the pressure appears in this expression, the equilibrium constant $K(T)$ is not a function of pressure. Rather it is ξ that is a function of pressure. The greater the total pressure, the smaller ξ must be to compensate. This is an example of Le Chatelier's principle: If a chemical reaction at equilibrium is subjected to a change in conditions that displaces it from equilibrium, then the reaction adjusts toward a new equilibrium state in such a way as to minimize the effect of the change. In other words, if we increase the total pressure, the equilibrium shifts in the direction of fewer moles of total components (toward the left in the present reaction). This minimizes the total pressure, thus acting to minimize the effect of the change.

Example: we consider once again the reaction



for which $K(T) = 1.36 \times 10^{-3}$ at 298 K. Determine the extent of reaction x at equilibrium at a pressure of 1 millibar and at a pressure of 1 bar.

SOLUTION: We construct a table

| | | |
|--------------------------|-----------------------------|-----------------------------|
| $\text{NH}_3 (\text{g})$ | $3/2 \text{H}_2 (\text{g})$ | $1/2 \text{N}_2 (\text{g})$ |
| $1 - \xi$ | $3/2\xi$ | $1/2\xi$ |

The total number of moles is $1 - \xi + 3/2\xi + 1/2\xi = 1 + \xi$. Dalton's law tells that the partial pressure of each gas is

| | | |
|--------------------------|-----------------------------|-----------------------------|
| $\text{NH}_3 (\text{g})$ | $3/2 \text{H}_2 (\text{g})$ | $1/2 \text{N}_2 (\text{g})$ |
| $(1 - \xi)P/(1+\xi)$ | $3/2\xi P/(1+\xi)$ | $1/2\xi P/(1+\xi)$ |

We substitute these expressions into the equilibrium constant.

$$\begin{aligned}
 K(T) &= \frac{(P_{H_2})^{3/2} (P_{N_2})^{1/2}}{(P_{NH_3})} = \frac{\left(\frac{3/2\xi P}{1+\xi}\right)^{3/2} \left(\frac{1/2\xi P}{1+\xi}\right)^{1/2}}{\left(\frac{(1-\xi)P}{1+\xi}\right)} \\
 &= \frac{\left(\frac{3}{2}\right)^{3/2} \left(\frac{1}{2}\right)^{1/2} \left(\frac{\xi P}{1+\xi}\right)^2}{\left(\frac{(1-\xi)P}{1+\xi}\right)} = \frac{\left(\frac{3}{2}\right)^{3/2} \left(\frac{1}{2}\right)^{1/2} \xi^2 P}{(1-\xi^2)}
 \end{aligned}$$

Now we solve for ξ

$$\xi = \sqrt{\frac{K}{K + 0.569P}}$$

As P gets large we can see that ξ gets small. This is in accord with Le Chatelier's principle since the number of moles of all components will be reduced as the equilibrium is shifted to the left.

If P = 1 mbar then

$$\xi = \sqrt{\frac{1.36 \times 10^{-3}}{1.36 \times 10^{-3} + 0.569(0.001)}} = 0.839$$

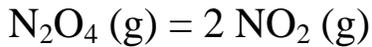
And if P = 1 bar

$$\xi = \sqrt{\frac{1.36 \times 10^{-3}}{1.36 \times 10^{-3} + 0.569(1)}} = 0.049$$

Given the relation $\Delta_r G^\circ = -RT \ln K(T)$ it is also possible to calculate equilibrium constants from tabulated standard molar Gibbs energy data. We simply invert the relation to find $K(T) = \exp\{-\Delta_r G^\circ/RT\}$.

We can plot the Gibbs energy, G versus the extent of reaction, ξ . This plot will pass through a minimum at the equilibrium

composition or extent of reaction. This is treated concretely by considering the thermal decomposition of N_2O_4 (g)



Starting initially with an idealized one mole of N_2O_4 , as the reaction proceeds the number of moles will be $1 - \xi$ of N_2O_4 and 2ξ of NO_2 . The Gibbs energy of the reaction mixture is given by

$$\begin{aligned} G(\xi) &= (1 - \xi)G_{N_2O_4} + 2\xi G_{NO_2} \\ &= (1 - \xi)G_{N_2O_4}^{\circ} + 2\xi G_{NO_2}^{\circ} + (1 - \xi)\ln P_{N_2O_4} + 2\xi \ln P_{NO_2} \end{aligned}$$

The reaction is carried out at a constant total pressure of one bar (i.e. $P_{Total} = 1$). Therefore,

$$P_{N_2O_4} = x_{N_2O_4} P_{Total} = x_{N_2O_4}$$

$$P_{NO_2} = x_{NO_2} P_{Total} = x_{NO_2}$$

and we can calculate the mole fractions as we did above by determining the total number of moles present for any given extent of the reaction as $(1 - \xi) + 2\xi = 1 + \xi$.

$$x_{N_2O_4} = \frac{1 - \xi}{1 + \xi}, \quad x_{NO_2} = \frac{2\xi}{1 + \xi}$$

Choosing the standard states such that $\Delta_f G_{N_2O_4}^{\circ} = G_{N_2O_4}^{\circ}$ and $\Delta_f G_{NO_2}^{\circ} = G_{NO_2}^{\circ}$, the free energy expression becomes

$$G(\xi) = (1 - \xi)\Delta_f G_{N_2O_4}^{\circ} + 2\xi\Delta_f G_{NO_2}^{\circ} + (1 - \xi)RT \ln\left(\frac{1 - \xi}{1 + \xi}\right) + 2\xi RT \ln\left(\frac{2\xi}{1 + \xi}\right)$$

Substituting in the values

$$\Delta_f G_{N_2O_4}^{\circ} = 97.787 \text{ kJ/mole}$$

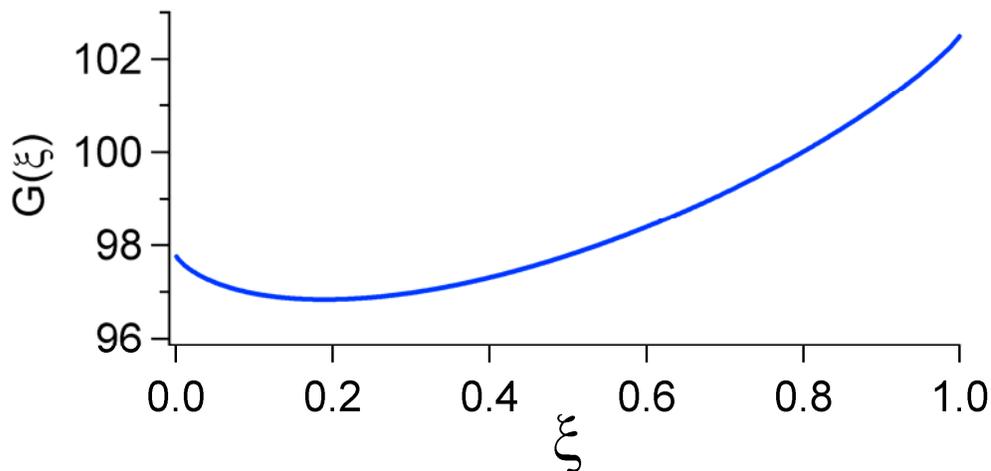
$$\Delta_f G_{NO_2}^{\circ} = 51.258 \text{ kJ/mole}$$

$$RT = 2.479 \text{ kJ/mole at } 298 \text{ K}$$

the equation becomes

$$G(\xi) = (1 - \xi)97.787 + 2\xi 51.258 + 2.479 \left[(1 - \xi) \ln\left(\frac{1 - \xi}{1 + \xi}\right) + 2\xi \ln\left(\frac{2\xi}{1 + \xi}\right) \right]$$

In principle, we could find the minimum of this function by taking the derivative with respect to ξ and setting the result equal to zero. This is very messy. An easy way to see that this function passes through a minimum is to plot it. A plot of the function is shown below.



We can determine graphically that the minimum occurs at $\xi_{\text{eq}} = 0.1892$. The equilibrium constant is given by

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{4\xi^2/(1+\xi)^2}{(1-\xi)/(1+\xi)} = \frac{4\xi^2}{1-\xi^2} = 0.148$$

This is exactly the same value that we obtain if we calculate the equilibrium constant using the free energy of the reaction.

$$\Delta_r G^\circ = 2\Delta_f G^\circ_{\text{NO}_2} - \Delta_f G^\circ_{\text{N}_2\text{O}_4} = -47.290 \text{ kJ/mole}$$

From $K(T) = \exp\{-\Delta_r G^\circ/RT\}$ we obtain $K(T) = 0.148$.

The ratio of the reaction quotient to the equilibrium constant determines in which direction the reaction will proceed. We have seen that the general expression for the free energy of reaction is

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

and that at equilibrium

$$\Delta_r G^\circ = -RT \ln K.$$

Therefore,

$$\Delta_r G = -RT \ln K + RT \ln Q = RT \ln(Q/K)$$

According to this equation $\Delta_r G = 0$ and the system is at equilibrium when $Q = K$. If $Q < K$, $\Delta_r G < 0$ and the reaction proceeds spontaneously in the forward direction. Returning to our generic reaction this means that A and B are converted in Y and Z.



This means that reactants will continue to form products until the minimum in the Gibbs energy is reached. On the other hand, if $Q > K$, $\Delta_r G > 0$ and the reaction proceeds spontaneously in the reverse direction. In this case Y and Z react to form A and B.

Note that it is the sign of $\Delta_r G$ that determines the spontaneous direction. The standard free energy of reaction, $\Delta_r G^\circ$ determines the equilibrium constant, but does not predict how the reaction will proceed. The direction depends on the amount of reactants and products present at a given extent of reaction. The free energy $\Delta_r G$ reflects the spontaneous direction given the composition of reactants and products at a given ξ .

In this course we have not considered the van't Hoff equation for the temperature dependence of the free energy. Likewise, for the temperature dependence of the equilibrium constant we will rely on the temperature dependence of $\Delta_r G^\circ(T)$ that we have already discussed in terms of temperature dependent enthalpy, $\Delta_r H^\circ(T)$ and entropy, $\Delta_r S^\circ(T)$. Once the free energy, $\Delta_r G^\circ(T)$ has been calculated at the temperature of interest we can always obtain the equilibrium constant from $K(T) = \exp\{-\Delta_r G^\circ/RT\}$.