Chapter 47   FREE ENERGY AND EQUILIBRIUM

We have seen examples dealing with standard conditions and examples dealing with nonstandard conditions, and how the initial conditions can impact the value of ΔG. Furthermore, these changes can also change the sign of ΔG and therefore the direction the reaction can take. But there is another consideration with important ramifications: while a reaction is actually occurring, the amounts of reactants and products are steadily changing and therefore Q itself is changing. Thus, during the reaction itself, ΔG is changing; in fact, it is heading towards zero. The direction of allowed, net change is ALWAYS towards balance, towards equilibrium. At equilibrium, $\Delta G = 0$ and there is no further net change. This has very important consequences.

47.1 Equilibrium aspects

Let's consider the special case of equilibrium conditions. Recall Case 3 from Section 45.3.

" • CASE 3 ΔS_{univ} IS ZERO which means ΔG_{sys} IS ZERO.
            S_{univ} stays the same.
            G_{sys} stays the same.

This is a very special Case. It's a very important Case. The reaction as written cannot happen by itself and the reverse reaction cannot happen by itself. Although neither can happen by themselves, BOTH can happen together as long as they happen <u>to the same extent</u>. Both directions are in balance. Sound familiar? THIS IS EQUILIBRIUM. $\Delta G_{sys} = 0$ is the equilibrium condition. "

We can now connect the equilibrium condition to our general Q equation by setting $\Delta G = 0$.

at equilibrium: $\Delta G = 0 = \Delta G° + RT \ln Q$

Re-arrange.

at equilibrium: $\Delta G° = -RT \ln Q$

This relationship has important consequences. For a given reaction at a given temperature, $\Delta G°$ is a constant. Since $\Delta G°$, R and T are constants in this equation, then the reaction quotient itself is a constant at equilibrium. This has special significance, and a new term is introduced: the equilibrium quotient or equilibrium constant, symbolized by K. The equilibrium constant is the reaction quotient at equilibrium conditions.

$$\Delta G° = -RT \ln K$$

For a given reaction at a given temperature, this provides a direct relationship between the change in standard free energy of the process and the equilibrium quotient. We can also re-arrange this equation and solve for K by the exponential (antiln) function.

$$K = e^{-\Delta G°/RT}$$

Thus, with either equation, we can find $\Delta G°$ from K and vice versa. You need to be able to work with either equation and be able to convert in either direction.

You must understand the distinction between Q and K. K is simply one specific condition of Q. For any reaction, Q can be any value and it will depend on the conditions (activities) which apply. K, however, is specific to the equilibrium condition; it is a fixed value for a specific T and that value also connects to $\Delta G°$ by the relationship above. Q will equal K at the equilibrium condition of balance, but Q can be lots of other values when not at equilibrium. As noted in the last Chapter, Q can also equal one if all reactants and products are at standard conditions. Let's summarize the variations for Q.

For any condition: Q = reaction quotient for the given conditions

For standard condition: $Q = 1$

For equilibrium condition: $Q = K$

In general, the numerical value of Q can vary widely. However, for the specific case of standard conditions, the value is 1 (exact); for the specific case of equilibrium balance, the value is equal to K.

The equilibrium constant, K, has major significance and we shall see many cases of that in many Chapters to come. For now, we will apply it to various equilibria which we have considered so far. As

noted, you can use K to find $\Delta G°$ or you can use $\Delta G°$ to find K. Let's consider five reactions/processes from the last Chapter and then we'll throw in a new twist for Example 6.

. . . .

Example 1. $\qquad$ $2\,NO(g)\ +\ 2\,Cl_2(g)\ \rightleftharpoons\ 2\,Cl_2O(g)\ +\ N_2(g)$
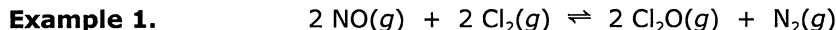
Let's say you measured the contents of the system at equilibrium (at 298.15 K) and found that K = 0.000213. What is $\Delta G°$ for the reaction?

. . . .

You need

$$\Delta G° \ = \ -RT\,\ln K$$

for which

$$\Delta G° \ = \ -(8.314\ \text{J/K})(298.15\ \text{K})\ \ln(0.000213)\ =\ 21{,}000\ \text{J}\ =\ 21.0\ \text{kJ}$$

and there's your $\Delta G°$. We worked with the value $\Delta G°$ = 20.96 kJ in Example 3 from last Chapter. The two values are the same to the correct sigfigs.

This calculation now provides a third method for the determination of a $\Delta G°$, in addition to the prior methods from $\Delta H° - T\Delta S°$ and from $\Delta G_f°$. This new method is important because it is often convenient to measure the amounts of components in a system at equilibrium, which then provides a measure of K and then of $\Delta G°$.
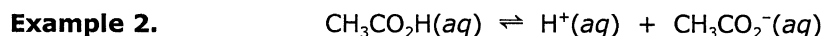
Now keep in mind that K, like Q, is products-over-reactants and it has no units. K expressions are the same as Q expressions.

$$K \ = \ \frac{P(Cl_2O)^2\ P(N_2)}{P(NO)^2\ P(Cl_2)^2}$$

At equilibrium, this ratio of products over reactants has the numerical value of K = 0.000213.

Next.

. . . .

Example 2. $\qquad$ $CH_3CO_2H(aq)\ \rightleftharpoons\ H^+(aq)\ +\ CH_3CO_2^-(aq)$

Let's say this solution was set up with a bit of strong acid added in order to vary the amount of H^+. Now let's say that you measured the following concentrations at equilibrium.

$$[CH_3CO_2H]\ =\ 0.165\ M \qquad [H^+]\ =\ 0.00224\ M \qquad [CH_3CO_2^-]\ =\ 0.00130\ M$$

Find $\Delta G°$ for the weak acid dissociation at 298.15 K.

. . . .

You can do this one. You need to set up the K expression, plug in the equilibrium quantities and solve for the numerical value of K.

K expression $\qquad\qquad$ measured conditions

$$K\ =\ \frac{[\underline{\qquad\qquad}]\,[\underline{\qquad\qquad}]}{[\underline{\qquad\qquad}]}\ =\ \frac{(\underline{\qquad\qquad})(\underline{\qquad\qquad})}{(\underline{\qquad\qquad})}\ =\ \underline{\qquad\qquad}...$$

Use K to calculate the $\Delta G°$.

$$\Delta G°\ =\ -RT\,\ln K\ =\ -(\underline{\qquad\qquad})(\underline{\qquad\qquad})\ \ln(\text{above number }K)\ =\ \underline{\qquad\qquad}\ \text{kJ}$$

Plug in, punch out, round off. You will need to decimal shift three places to end up in kJ. You can check your final answer by referring to Example 5 in Chapter 46, although you get one less decimal place here. (Be sure to compare to $\Delta G°$ and not just ΔG in the Chapter 46 Example.)

Now we'll turn things around and use $\Delta G°$ to solve for K. In doing so, we'll show some more connections and consequences.

We return to the vaporization of water.

$$H_2O(l)\ \rightleftharpoons\ H_2O(g)$$
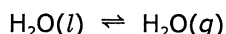
In the last Chapter, we talked about this quite a bit. For example,

❝ Using $\Delta H°_{vap}$ and $\Delta S°_{vap}$ from the illustration upstairs, you would find $\Delta G°_{vap}$ = 8.56 kJ. That's endergonic. Evaporation of water cannot happen by itself <u>under the given conditions</u>. But water does evaporate at 25 °C. We know that from common experience. How can water evaporate at 25 °C if evaporation is endergonic at these conditions? ❞

and

❝ We consider a container system which has an overhead gas space containing one mol $H_2O(g)$ with P = one atm and one mol of pure $H_2O(l)$ in the bottom of the container.

$$H_2O(l) \;\rightleftharpoons\; H_2O(g) \qquad \Delta G°_{vap} \;=\; 8.56 \text{ kJ}$$
$$\text{one atm}$$

At these conditions, the sign of $\Delta G°_{vap}$ is positive and the forward process is endergonic; more vaporization cannot happen by itself. However, the reverse process, condensation, is allowed. Net change can happen in the reverse direction: this decreases P of $H_2O(g)$ until the system hits equilibrium. At equilibrium, there will be less than one mol of $H_2O(g)$ and the pressure of $H_2O(g)$ will be less than one atm. In fact, that pressure is water's EVP at 25 °C and that value is 0.0313 atm. Also at equilibrium, there will be more than one mol of $H_2O(l)$. ❞

Let's now derive this EVP from thermodynamic values.

. . . .

Example 3. Calculate the EVP for water at 25.00 °C from $\Delta G°_{vap}$.

. . . .

We have our equation and the $\Delta G°_{vap}$ in the above quotes. We need

$$K \;=\; e^{-\Delta G°/RT}$$

and you're ready to go. Here's just the exponent term so far.

$$\frac{-\Delta G°}{RT} \;=\; \frac{-(8.56 \text{ kJ})}{(8.314 \text{ J/K})(298.15 \text{ K})}$$

OK, you need to be careful with units again. The kelvins drop out just fine, but there's a kJ in the numerator and a J in the denominator. One of those needs to decimal shift and it doesn't matter which. I'll shift the numerator.

$$\frac{-\Delta G°}{RT} \;=\; \frac{-8,560 \text{ J}}{(8.314 \text{ J/K})(298.15 \text{ K})}$$

Now plug all that in and punch it out: you get –3.4532..., but we're not done yet. You still have to take the antiln of that to get to your final K.

$$K \;=\; e^{-3.4532...} \;=\; 0.0316$$

OK, so you now have the value of K. What does that tell you? Well, what does K itself mean for this example? What is the K expression?

$$K \;=\; P(H_2O(g))$$

This K is the activity of $H_2O(g)$ at equilibrium; this activity represents the pressure in atm at equilibrium, so this result gives the value for EVP (in atm). Thus, using a $\Delta G°_{vap}$ for any substance, we can calculate an EVP for that substance. You can even calculate an EVP at other temperatures via $\Delta G°_{vap} = \Delta H°_{vap} - T \Delta S°_{vap}$. Notice that our calculated value here (0.0316 atm) differs a tad from the value quoted above from Chapter 46 (0.0313 atm), but that's good enough within the given sigfigs.

Next.

. . . .

Example 4. $C_4H_9OH(l) \;\rightleftharpoons\; C_4H_9OH(aq)$

In Chapter 46 Example 2, we had $\Delta G°_{soln}$ = –0.17 kJ for dissolving 1-butanol in water. Now, find K and the solubility of 1-butanol in water at 25.00 °C.

. . . .

You need

$$K \;=\; e^{-\Delta G°/RT}$$

Focus first on the exponent part.

$$\frac{-\Delta G°}{RT} = \frac{-(-0.17 \text{ kJ})}{(8.314 \text{ J/K})(298.15 \text{ K})}$$

Decimal shift the numerator. While you're at it, watch the signs: you have two negatives in the numerator on the right which we'll just leave out.

$$\frac{-\Delta G°}{RT} = \frac{170 \text{ J}}{(8.314 \text{ J/K})(298.15 \text{ K})}$$

Punch all of that out and you get 0.068581...; do the antiln to get to the final K.

$$K = e^{0.068581...} = 1.1$$

There's your value for K but what does that tell us? Consider the K expression.

$$K = [C_4H_9OH(aq)]$$

This gives the activity of 1-butanol in water at equilibrium, which corresponds to the concentration in M. This result is the solubility of 1-butanol in water. The calculated value of K says that the equilibrium (saturation) concentration for 1-butanol in water is 1.1 M.

Your turn.

. . . .

Example 5. Find the solubility (in M) of pentane, C_5H_{12}, in water.

$$C_5H_{12}(l) \rightleftharpoons C_5H_{12}(aq)$$
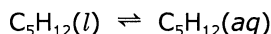
In Section 39.4, we had $\Delta H°_{soln} = -1.9$ kJ. In Section 44.2, we listed $\Delta S°_{soln} = -68.2$ J/K. Find $\Delta G°_{soln}$ from these at 25.00 °C and use that to find the solubility at 25.00 °C.

. . . .

Do the $\Delta G°_{soln}$ part.

Then $K = e^{-\Delta G°/RT}$.


Now what is the K expression?

The numerical value for K is the concentration (in M) of C_5H_{12} dissolved in water at equilibrium. The number is certainly small enough for pentane to be classified as insoluble. If you want to check your answers, they're in Section 51.2.

With the water EVP example and the two solubility examples, we are seeing a valuable application for K. I should point out, however, that we are still assuming ideal behavior and I should remind you that solutions are more prone to nonideal behavior than are gases at common conditions. The Examples above are very good for matching ideal and real behavior but high concentrations will not be. Furthermore, for ionic solutes, only very small concentrations will give a good agreement between real and ideal.

OK, let's add one more twist to this process. We'll revisit carbonation from Section 41.2. Instead of a flavored beverage, we'll just work with CO_2 and water.

. . . .

Example 6. Calculate the solubility (in M) of CO_2 in water at 25.00 °C when the equilibrium pressure of $CO_2(g)$ above the solution is 4.0 atm.

. . . .

Where to start? Like always, start with an equation.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
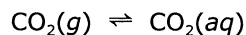
What does that get you? Well, what does K look like?

$$K = \frac{[CO_2(aq)]}{P(CO_2(g))}$$

In this problem, you are given the pressure of the overhead $CO_2(g)$ at equilibrium, and you are looking for the concentration of $CO_2(aq)$ (in M). Let's re-arrange.

$$[CO_2(aq)] = K \times P(CO_2(g))$$

Hmmm. Wait a minute. Does that look vaguely familiar? Section 41.2: it's the gas solubility equation. At that time, we considered the solubility of some gas compound A in water and the equation was written as follows.

$$[A(aq)] = k_H \times P_A$$

The gas solubility equation was developed from experimental observations many, many years ago and now we have the same equation derived from thermodynamic principles. This also provides a thermodynamic connection for the values of k_H. A primary difference between K and k_H is that K uses activities which are unitless while k_H traditionally carries units directly. There can also be differences between the numerical values of K and k_H when conditions are not so ideal or when other processes are operating but, for simple solubility, the values of K and k_H will be equal or very close.

Continuing now, you were given $P(CO_2(g))$. You need the value for K and that will come from ΔG°_{soln} which is hereby provided as $\Delta G^\circ_{soln} = 8.41$ kJ. Calculate K.

$$K = e^{-\Delta G^\circ/RT} =$$

Then plug that in to get the solubility of $CO_2(aq)$.

$$[CO_2(aq)] = K \times P(CO_2(g)) = K \times 4.0$$

Since that is simply a re-arranged K expression, the pressure activity is entered as unitless. Now, solve for $[CO_2(aq)]$.

This will give the number for the solubility of CO_2 at these conditions and that will be a molarity. That molarity is your fizz factor for a freshly-opened bottle of carbonated water.

With these six Examples, we see the vital connection between K and ΔG°. These Examples provide a small introduction to the many important consequences from this relationship. We will develop much more of K beginning in Chapter 51 and continuing through Chapter 60. The impact is huge, but that is the nature of equilibrium anyway. Equilibrium is an essential aspect which carries impact on all processes, small and large. It's an important part of you, it's an important part of your world. Equilibrium is balance. Equilibrium is also the net stopping point, and that was part of the drive to bring you here.

47.2 Drive

We are closing on four Chapters which have addressed the question of whether a reaction or process can or cannot happen. If it can happen, then the next question becomes to what extent: can the reaction go to completion, L→R, or does it go to some point of equilibrium in between, ending with a mixture of all reagents from both sides of the equation? These are vastly important questions. Ultimately, the outcome is dictated by the various contributions to the change in total entropy, ΔS_{univ}, which we have tidily packaged into the system parameter of ΔG.

Remember that there are two important parts of ΔG. The first is the sign of ΔG and this part determines the allowed direction: a negative ΔG says the reaction is allowed in the forward direction, L→R, while a positive ΔG says the reaction is allowed in the reverse direction, L←R. The second important part is the magnitude of the ΔG. This is the energy which would be available from the exergonic process or this is the minimum payment into the system which would be required for an endergonic process. Traditionally, for an exergonic process, this has also been called the "driving force". The driving force represents Nature's drive toward maximum S_{univ}. When there are more and more options to be gained, then ΔS_{univ} is larger and larger and ΔG is more and more negative. A more negative ΔG has a greater driving force to happen; a less negative ΔG has a smaller driving force to happen.

Let's put some of this to picture.

Consider a simple equilibrium involving gases A and Z, in a 1:1 rxn ratio.

$$A(g) \rightleftharpoons Z(g)$$
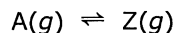
We can start with 1.00 atm of A and no Z, or we can start with no A and 1.00 atm of Z, or we can start anywhere in-between. The free energies involved at different compositions in the system are depicted at right. (Note that the vertical axes represent values of G, and not of ΔG. A change in free energy, ΔG, will be the difference between two G's on the curve.) The condition of 1.00 atm of A and no Z is depicted at the far left on the horizontal axis, and the free energy of this system is designated G_A. Conversely, the condition of no A and 1.00 atm of Z is depicted at the far right, and the free energy of this system is designated G_Z. Any point on the curve between the two vertical axes represents the free energy for a system containing a mixture of A and Z. Nature drives to maximum S_{univ} which corresponds to the minimum G of the system. The minimum G is the equilibrium point, designated G_{eq}. For this illustration, equilibrium occurs when the system contains 0.36 atm of A and 0.64 atm of Z, which gives K = 1.8. Regardless of where we start, the final, net stopping point for the system is the point of equilibrium.
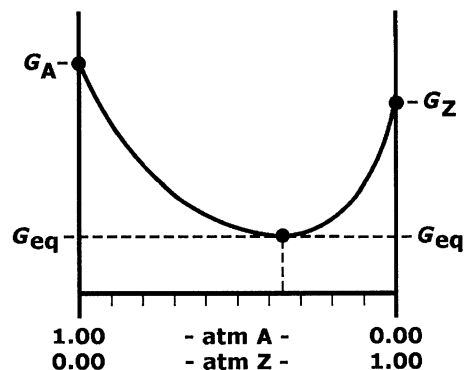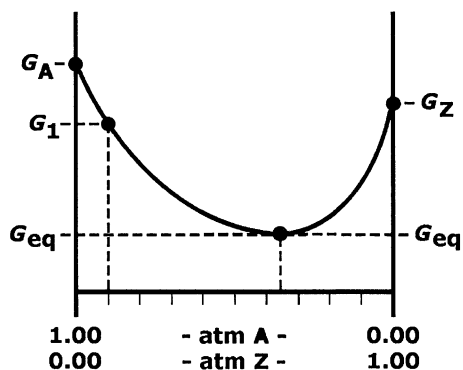
If we start with 1.00 atm of A and no Z and let that go to equilibrium, the change in free energy from G_A to G_{eq} (hereby designated ΔG_A) is

$$\Delta G_A = G_{final} - G_{initial} = G_{eq} - G_A$$

and this will be negative, because $G_{eq} < G_A$. At the other extreme, if we start with no A and 1.00 atm of Z and let that go to equilibrium, then the change in free energy (hereby designated ΔG_Z) is

$$\Delta G_Z = G_{final} - G_{initial} = G_{eq} - G_Z$$

and this will also be negative, because $G_{eq} < G_Z$. Either way, the allowed direction has a negative ΔG.

Now let's say you start the reaction with 1.00 atm of A and no Z, and let it run a bit until you have a mixture of 0.90 atm of A and 0.10 atm of Z. This point is added at left, with G_1 indicating the free energy for this new set of conditions. Going from that point on to equilibrium, the change in free energy, ΔG_1, is given by

$$\Delta G_1 = G_{final} - G_{initial} = G_{eq} - G_1$$

and this will again be negative (because $G_{eq} < G_1$). Note that ΔG_1 is less negative than the original ΔG_A; as the reaction proceeds L→R, ΔG takes on smaller negative values, corresponding to a decrease in the driving force. Note also that the given amounts correspond to Q = 0.10/0.90 = 0.11, and Q is less than K; as the reaction proceeds towards equilibrium, Q will increase.

We can do this in the other direction also. Let's say you start the reaction with no A and 1.00 atm of Z, and let it run a bit until you have a mixture of 0.10 atm of A and 0.90 atm of Z. This is now illustrated at right, with G_2 representing the free energy for this new set of conditions. From that point on to equilibrium, the change in free energy, ΔG_2, is given by

$$\Delta G_2 = G_{final} - G_{initial} = G_{eq} - G_2$$

and this will again be negative (because $G_{eq} < G_2$). ΔG_2 is less negative than the starting ΔG_Z; as the reaction proceeds L←R, ΔG takes on smaller negative values and the driving force is again decreasing. Note also that the given amounts result in Q = 0.90/0.10 = 9.0, and Q is greater than K; as the reaction proceeds towards equilibrium, Q will decrease.
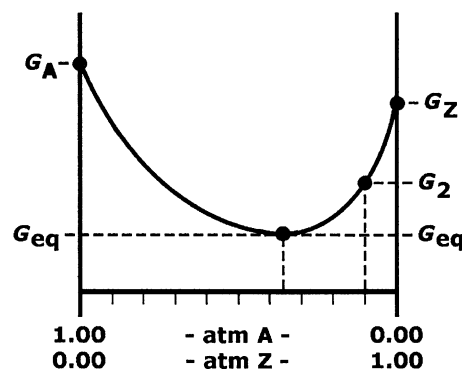
Regardless of whether the system begins at a point to the left or to the right of equilibrium, the allowed direction of net change is always toward equilibrium. Upon reaching equilibrium, there is no further net change, and ΔG = zero.

Here's another way of looking at the exergonic directions in the plots above: beginning from any point on the free energy curve to the left or to the right of equilibrium, the allowed direction is downhill because that leads to the minimum G for the system. At the point of equilibrium, the curve is horizontal with a zero slope; there is no downhill direction and there is no further net change. Conversely, if the system is starting at equilibrium or on either side of equilibrium, and you want to move it further away from equilibrium, then that's an uphill climb; that's endergonic, and you must pay into the process.

1.00   - atm A -   0.00
0.00   - atm Z -   1.00
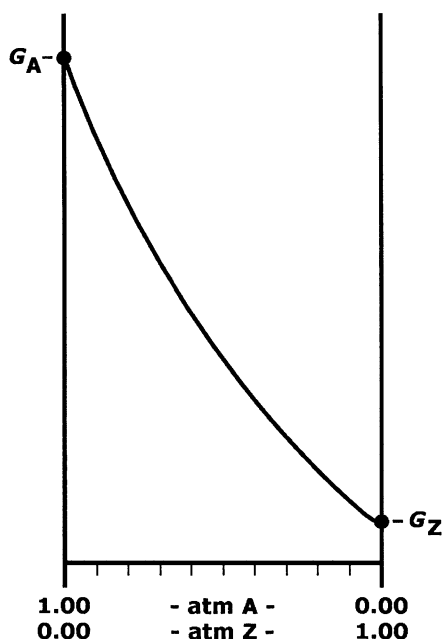
But not every process or reaction involves a significant equilibrium. In many cases, reactants react to completion, leaving only products in the system at the end of the reaction. These reactions will have a sizeably negative $\Delta G°$, corresponding to a very large value of K. Consider some such reaction which is exergonic in the L→R direction, as depicted at left.

$$A(g) \rightarrow Z(g)$$
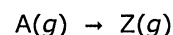
The minimum in the energy diagram essentially occurs all the way to the right. While you may be able to calculate an equilibrium amount remaining for A, it is negligible, and essentially only Z remains. This reaction would go to completion. Common combustion reactions are examples of this type. (If you want, you can take a sneak peak at Case D in Chapter 51 for an example.)

For any of the allowed processes described here, the driving force decreases as the reaction occurs. For any exergonic reaction, the greatest driving force (the most negative ΔG) occurs at the moment of starting the reaction. As the reaction proceeds, the driving force gets weaker (less negative ΔG) and eventually goes to zero.

Let's now look at an equilibrium system from a somewhat different perspective. Consider the progress of an equilibrium system in terms of the general ΔG equation.

$$\Delta G = \Delta G° + RT \ln Q$$

Let's consider Q in terms of rights-over-lefts.

$$\Delta G = \Delta G° + RT \ln \frac{R}{L}$$

For present illustration purposes, we specify that $\Delta G°$ is negative. We additionally specify that at least one solute or gas is present on both sides of the balanced equation and that the starting amounts of solutes and/or gases result in $Q < 1$ initially. For $Q < 1$, $\ln Q$ will be negative. Under these conditions, the ΔG will be negative and the reaction is exergonic in the forward direction, L→R. Once the reaction starts and as the reaction proceeds in this L→R direction, then we can note the following.

The amounts of products increase on the right and this increases the numerator of Q.
The amounts of reactants decrease on the left and this decreases the denominator of Q.
As a result, the value of Q = R/L increases.
The term, $RT \ln(R/L)$, increases (becomes less negative).
This makes ΔG less negative.
This means the driving force weakens.

This is reflected in the diagram at right which now introduces a time component. Initially, ΔG is some negative number at time zero; this becomes less negative as time goes on. Ultimately, the system reaches $\Delta G = 0$, and there is then no net driving force. Even though there can be some amount of each reagent on the left and on the right, there is no net change in their amounts. The reaction is "done".
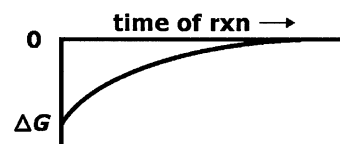
As we go along through the many Chapters addressing the question of what <u>can happen</u>, we are also developing the fuller picture of equilibrium. Recall what was said in Chapter 35.

 ❝ There are two approaches to describe the balance which is associated with any equilibrium.

  1. The first approach is by the speeds (rates) of the opposing processes. At the point of equilibrium, these speeds are equal and in balance. This approach is the kinetic description of equilibrium.

  2. The second approach is by enthalpy and entropy. At the point of equilibrium, a system's enthalpy and its entropy are in balance. This approach is the thermodynamic description of equilibrium.

 As I said, these two items are really big for all equilibria in general. Write "THE BIG TWO" in the margin next to them. ❞

Now, here in Chapter 47, we have completed the second of The Big Two with respect to <u>can happen</u>. There will be more of equilibrium down the road but, for now, we turn to the other side of the story regarding whether something <u>will happen</u>. Keep in mind that, even though a process is allowed, it does not mean that it will really happen. An exergonic reaction in a beaker with a small driving force may go to equilibrium or it may never happen. A possible explosion with a huge driving force may go to completion or it may never happen. Whether an exergonic process will actually happen or will not happen is an entirely separate issue, and that will connect into the first of The Big Two. That is where we go next.

 It's time to get the ball rolling.

Problems

1. True or false.

 a. For every reaction, the direction of allowed net change is toward $\Delta G = 0$.

 b. For any process at equilibrium, $K = 1$.

 c. The greatest driving force for any exergonic process is at the very start of the process.

 d. As Q increases, the driving force increases.

2. Which one of the following is an equilibrium condition for every reaction?

 a. $Q > K$ b. $Q = K$ c. $Q < K$ d. $Q =$ one   e. $K = 0$

3. Consider the following balanced equation.

$$CO_2(g) + 6\,HI(g) \rightleftharpoons H_2O(g) + CH_3OH(g) + 3\,I_2(s)$$

 Find the value for K at 298.15 K.

4. Consider the following balanced equation.

$$Ba^{2+}(aq) + CO_2(g) + H_2O(l) \rightleftharpoons BaCO_3(s) + 2\,H^+(aq)$$

 Find the value for K at 298.15 K.

5. Consider the sublimation of $I_2(s)$.

 a. What is the EVP (in atm) of $I_2(g)$ at 25.00 °C?

 b. What is the EVP (in atm) of $I_2(g)$ at 65.00 °C?

6. Consider the solubility of $H_2S(g)$ in water. At 298.15 K, what is the equilibrium concentration (in M) of $H_2S(aq)$, if the overhead pressure of $H_2S(g)$ is 0.136 atm?