

Chapter 47 FREE ENERGY AND EQUILIBRIUM

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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 beyond simply changing the initial conditions: 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 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 during the process.
 G_{sys} stays the same during the process.”

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 to the same extent. Both directions are in balance. Sound familiar? THIS IS EQUILIBRIUM. $\Delta G_{\text{sys}} = 0$ is the thermodynamic statement of the equilibrium condition. ”

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

$$\text{at equilibrium:} \quad \Delta G = 0 = \Delta G^\circ + RT \ln Q$$

Re-arrange.

$$\text{at equilibrium:} \quad \Delta G^\circ = -RT \ln Q$$

This relationship has important consequences. For a given reaction at a given temperature, ΔG° is a constant. Since ΔG° , 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.

$$\Delta G^\circ = -RT \ln K$$

For a given reaction at a given temperature, this provides a direct relationship between the 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.

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

Thus, with either equation, we can find ΔG° 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 ΔG° 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

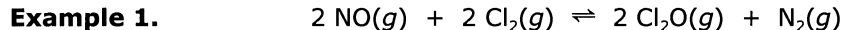
For standard condition: $Q = 1$

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 ΔG° or you can use ΔG° to find K . Let's re-consider five Examples from the last Chapter and then we'll throw in a twist for Example 6.



Let's say you measured the contents of the system at equilibrium (at 298.15 K) and found that $K = 0.000213$. What is ΔG° for the reaction?

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You need

$$\Delta G^\circ = -RT \ln K$$

for which

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

and there's your ΔG° .

This calculation now provides a third method for the determination of a ΔG° , in addition to the prior methods from $\Delta H^\circ - T \Delta S^\circ$ and from ΔG_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 ΔG° .

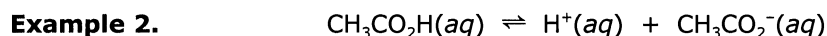
Now keep in mind that K , like Q , is products-over-reactants and it has no units. K expressions are the same as Q expressions.

$$K = \frac{P(\text{Cl}_2\text{O})^2 P(\text{N}_2)}{P(\text{NO})^2 P(\text{Cl}_2)^2}$$

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

Next.

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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.

$$[\text{CH}_3\text{CO}_2\text{H}] = 0.165 \text{ M} \quad [\text{H}^+] = 0.00224 \text{ M} \quad [\text{CH}_3\text{CO}_2^-] = 0.00130 \text{ M}$$

Find ΔG° for the weak acid dissociation.

.....

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	measured conditions
$K = \frac{[\text{ }][\text{ }]}{[\text{ }]}$	$= \frac{(\text{ })(\text{ })}{(\text{ })} = \text{.....}$

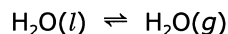
Use K to calculate the ΔG° .

$$\Delta G^\circ = -RT \ln K = -(\text{ })(\text{ }) \ln(\text{above number } K) = \text{..... kJ}$$

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 ΔG° and not just ΔG in the Chapter 46 example.)

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

We return to the vaporization of water.



In the last Chapter, we talked about this quite a bit. For example,

“ Using $\Delta H_{\text{vap}}^{\circ}$ and $\Delta S_{\text{vap}}^{\circ}$ from the example upstairs, you would find $\Delta G_{\text{vap}}^{\circ} = 8.56 \text{ kJ}$. That's endergonic. Evaporation of water cannot happen by itself under the given conditions. 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 the system to contain some $\text{H}_2\text{O}(l)$ and some $\text{H}_2\text{O}(g)$ whose $P = \text{one atm}$. At these conditions, the sign of ΔG° 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; P of $\text{H}_2\text{O}(g)$ can decrease until the system hits equilibrium. At equilibrium, there can be some $\text{H}_2\text{O}(g)$ but it will be less than one atm. That is water's EVP at 25 °C and that value is 0.0313 atm. ”

Let's now derive this from thermodynamic values.

Example 3. Calculate the EVP for water at 25.00 °C from $\Delta G_{\text{vap}}^{\circ}$.

We need

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

for which we'll use $\Delta G_{\text{vap}}^{\circ} = 8.56 \text{ kJ}$ as given in the quote. Here's just the exponent term so far.

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

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.

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

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

$$K = e^{-3.4532\dots} = 0.0316$$

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

$$K = P(\text{H}_2\text{O}(g))$$

This K is the activity of $\text{H}_2\text{O}(g)$ at equilibrium; this activity represents the pressure in atm at equilibrium, so this result gives EVP (in atm). Thus, using a $\Delta G_{\text{vap}}^{\circ}$ for any substance, we can calculate an EVP for that substance. You can even calculate an EVP at other temperatures from $\Delta G_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} - T \Delta S_{\text{vap}}^{\circ}$. Notice that our calculated value here (0.0316 atm) differs a tad from the value quoted above (0.0313 atm), but that's good enough within the given sigfigs.

Next.

Example 4. $\text{C}_4\text{H}_9\text{OH}(l) \rightleftharpoons \text{C}_4\text{H}_9\text{OH}(aq)$

In Chapter 46 we had $\Delta G_{\text{soln}}^{\circ} = -0.17 \text{ kJ}$ for dissolving 1-butanol in water. Now, find K and the solubility of 1-butanol in water at 25.00 °C.

You need

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

Focus first on the exponent part.

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

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

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

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

$$K = e^{0.068581\dots} = 1.1$$

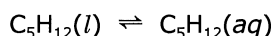
There's your K but what does that tell us? Consider the K expression.

$$K = [\text{C}_4\text{H}_9\text{OH}(aq)]$$

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. Find the equilibrium solubility of pentane, C_5H_{12} , in water.

Example 5.



In Section 39.4, we had $\Delta H_{\text{soln}}^\circ = -1.9 \text{ kJ}$. In Section 44.2, we derived $\Delta S_{\text{soln}}^\circ = -68.2 \text{ J/K}$. Find $\Delta G_{\text{soln}}^\circ$ from these and then find K at 25.00 °C.

Do the $\Delta G_{\text{soln}}^\circ$ part.

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

Now what is the K expression?

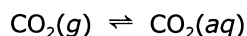
The numerical value for K is the concentration (in M) of C_5H_{12} dissolved in water at equilibrium. The number is certainly small enough for pentane to be classified as insoluble. If you want to check your answers, they're in Section 51.2.

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 pressure of $\text{CO}_2(g)$ above the solution is 4.0 atm.

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



What does that get you? Well, what does K look like?

$$K = \frac{[\text{CO}_2(aq)]}{P(\text{CO}_2(g))}$$

In this problem, you are given the pressure of the overhead $\text{CO}_2(g)$ and you are looking for the concentration of $\text{CO}_2(aq)$ (in M). Let's re-arrange.

$$[\text{CO}_2(aq)] = K \times P(\text{CO}_2(g))$$

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.

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

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 $P(\text{CO}_2(g))$. You need the value for K and that will come from $\Delta G_{\text{soln}}^\circ$ which is hereby provided as $\Delta G_{\text{soln}}^\circ = 8.41 \text{ kJ}$. Calculate K .

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

Then plug that in to get the solubility of $\text{CO}_2(aq)$.

$$[\text{CO}_2(aq)] = K \times P(\text{CO}_2(g)) = K \times 4.0$$

Since that is simply a re-arranged K expression, the pressure activity is entered as unitless. Now, solve for $[\text{CO}_2(aq)]$.

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, 2 L bottle of a typical carbonated beverage.

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 and which have also addressed some aspects of the equilibrium connection. Although the outcome is ultimately dictated by the change in total entropy, ΔS_{univ} , we have tidily packaged the entropy contributions into the system parameter of ΔG .

Remember that there are two parts of ΔG which are important. The first important part is the sign of ΔG and this part determines spontaneity: a negative ΔG says the reaction is allowed in the forward direction, $L \rightarrow R$, while a positive ΔG says the reaction is allowed in the reverse direction, $L \leftarrow R$. The second important part is the magnitude of the ΔG . This is the free 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.

But the driving force doesn't last forever. For any exergonic reaction, the greatest driving force (its 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. The driving force decreases as the

reaction proceeds because the value of Q is changing. We can see this in terms of the general ΔG equation.

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

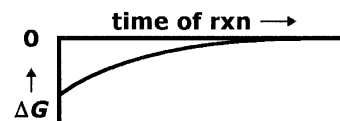
Let's rewrite Q in terms of rights-over-lefts.

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

For an illustration, let's say we set up some reaction for which ΔG° is negative and that the initial conditions give $Q < 1$. For $Q < 1$, $\ln Q$ will also be negative. With these assumptions, the overall ΔG will be negative and the reaction is exergonic in the forward direction, $L \rightarrow R$. Once the reaction starts and as the reaction proceeds in this direction $L \rightarrow R$, then

Products increase on the right and this increases the numerator of Q .
 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. Initially, ΔG is some negative number at time zero; this becomes less negative as time goes on. Ultimately, the system reaches $\Delta G = 0$ which is equilibrium; at this point $Q = K$.



I repeat part of the opening paragraph of this Chapter for emphasis.

...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 change is ALWAYS towards balance, towards equilibrium. At equilibrium, $\Delta G = 0$ and there is no further net change.

The natural drive for every process is toward $\Delta G = 0$ because, at this point, there are no further gains in entropy to be realized; thus, the driving force is zero. At equilibrium, the reaction is "done". This is the net stopping point overall, but it is NOT a point of total inactivity. The forward and reverse directions can still happen but they are equal and in balance.

As we go along through the many Chapters, we are yet developing the fuller picture of equilibrium. Compare to where we were in Chapter 35.

“ Furthermore, equilibrium is immensely important to many things in general. We first talked about equilibrium in Chapter 12.

As applied to chemical reactions, balance is called equilibrium... Chemical equilibrium will occur whenever opposing forces are operating within a chemical system. There will be a competition.

Here, we now apply these notions to phase changes. In the prior two paragraphs, I gave you two essential, key aspects which are very general to many equilibria, not just phase changes. This is really important stuff, so I want to emphasize this now. Pay very close attention.

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. It was also said in Chapter 35,

“ A system at equilibrium is definitely in motion. It just happens to be doing things in opposite directions at the same speed, which balances out. We refer to this motion as dynamic:

EQUILIBRIA ARE DYNAMIC. At the point of equilibrium, things are happening. The system is in motion but the motions are in balance.

Circle or highlight the last five sentences. Remember them. Understand them. These things are also extremely important to ALL equilibria in general, not just phases. ”

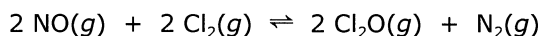
As we complete the answer to the question of "Can it happen?", we include its connection to equilibrium. Equilibrium is balance. It is the point of zero driving force. It is the final stopping point of net change for any process which can initially happen.

But so far, it's only been about what can happen. You must remember 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 happen or it may never happen. A possible explosion with a huge driving force may happen or it may never happen. Whether an exergonic process will actually happen or will not happen is an entirely separate issue, and that issue ties into the first of The Big Two. That is where we go next. Time to get the ball rolling.

Problems

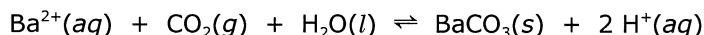
- True or false.
 - The greatest driving force for any exergonic process is at the very start of the process.
 - At equilibrium, $K = 1$.
 - For every spontaneous reaction, the drive is to reach $\Delta G = 0$.
- Which one of the following is an equilibrium condition for every reaction?
 - $Q > K$
 - $Q = K$
 - $Q < K$
 - $Q = \text{one}$
 - $K = 0$

- Consider the following balanced equation.



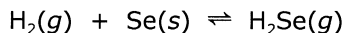
Find the value for K at 298.15 K.

- Consider the following balanced equation.



Find the value for K at 298.15 K.

- The following is the formation equation for hydrogen selenide, $\text{H}_2\text{Se}(g)$.



Find the value for K at 298.15 K.

- $\text{I}_2(s)$ sublimates at room temperature. What is the equilibrium vapor pressure (in atm) of $\text{I}_2(g)$ at 25.00 °C?
- The equilibrium vapor pressure of water at 40. °C is 55.4 Torr. Calculate $\Delta G_{\text{vap}}^\circ$ at this temperature.