

## Chapter 51

## GENERAL EQUILIBRIUM

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Having now seen whether something can/will/does happen, we now consider again where the process is going: equilibrium. Equilibrium is all about the balance and the factors which affect that balance. We started into this concept in Chapter 10 with solubility and then a bit with acids and bases in Chapter 11, although we didn't introduce the actual term until Chapter 12. We got heavily into equilibrium for phases beginning in Chapter 35 and for mixtures beginning in Chapter 41. We now continue equilibrium with a string of three Chapters devoted to more aspects of equilibria in general. In Chapters 54 - 60, we return to the water world, looking more deeply at several of the equilibria which lie immersed therein.

As noted in Section 47.2, all reactions are "done" when  $\Delta G = 0$ . Many reactions such as typical combustions do go completely to product to reach  $\Delta G = 0$ , but many other reactions are equilibrium processes. For these, the reaction comes to a point of balance with all reactants and products present in some amounts, whether those amounts are large or small. Equilibrium processes are vastly important to many aspects of your world, including you and your own cells. In every biological system, many reactions are equilibrium processes.

As we continue on this path, our emphasis will lie primarily in the thermodynamics of equilibrium and less so in the kinetics. Yes, kinetics will still dictate whether we will actually hit equilibrium or not within some reasonable timeframe, but our approach nevertheless focuses on the thermodynamic side of the story. Thus, for our purposes in the here and now, we assume that the kinetics does enable the system to reach its equilibrium within a reasonable time.

Also as we go, we turn more to the math involved in equilibrium and its calculations. Although the mathematical side will come more into play, the concepts behind the math remain important.

### 51.1 More $Q$ and $K$

Let's revisit several key points of thermodynamics which are related to equilibrium. From Chapters 46 and 47, we have the following.

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

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

We can insert the latter into the former to get

$$\Delta G = -RT \ln K + RT \ln Q$$

which re-arranges to

$$\Delta G = RT \ln \frac{Q}{K}$$

and this is yet another useful relationship. As we go, keep in mind the difference between  $Q$  and  $K$ . Chapter 47:

“ 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  $\Delta G^\circ$  by the relationship above.  $Q$  will equal  $K$  at the equilibrium condition of balance, but  $Q$  can also 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 calculated for the given conditions

For standard condition:  $Q = 1$

For equilibrium condition:  $Q = K$  ”

Above, we just derived a direct  $Q/K$  relationship which will provide another viewpoint. For example, for  $Q = K$  at equilibrium, then  $Q/K = 1$  and we have

$$\Delta G = RT \ln \frac{Q}{K} = RT \ln(1) = 0$$

which we already knew but which is yet another way to show how all of these aspects are connected.

Here's another consideration. In Section 47.2, we noted that a system has its greatest driving force (most negative value for  $\Delta G$ ) at the very beginning of the reaction. The system can then proceed in the exergonic direction. As the reaction proceeds, the driving force lessens and  $\Delta G$  becomes less negative. Ultimately,  $\Delta G$  is going to zero. Now apply this to the  $Q/K$  relationship.

$$\Delta G = RT \ln \frac{Q}{K}$$

In this equation,  $R$  is always a constant and, for a fixed  $T$ ,  $K$  is also constant; the only things changing are  $\Delta G$  and  $Q$ . As a reaction proceeds in its exergonic direction,  $\Delta G$  starts negative but is going to zero

$$\Delta G \rightarrow 0$$

so

$$RT \ln \frac{Q}{K} \rightarrow 0$$

or

$$\ln \frac{Q}{K} \rightarrow 0$$

and this means that  $Q/K$  itself is going to one

$$\frac{Q}{K} \rightarrow 1$$

which leads to

$$Q \rightarrow K$$

and this is also an important result. As the reaction proceeds, the reaction quotient  $Q$  is going towards the equilibrium quotient  $K$ . Thus, we can restate  $Q$  and  $K$  as follows.

$Q$  is where the system is at some point in time.  
 $K$  is where the system is heading.

Know these.

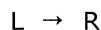
The relationship of  $Q$  to  $K$  now provides another indicator of the exergonic direction. At the start of some reaction with some set of given conditions,  $Q$  can be less than or greater than  $K$ . THE EXERGONIC DIRECTION IS THAT DIRECTION WHICH LEADS TO EQUILIBRIUM,  $Q = K$ . We now bring back the rights-over-lefts notation for  $Q$  (Section 47.2).

$$Q = \frac{R}{L}$$

$R$  represents the activities of the reagents on the right side of the balanced equation and  $L$  represents the activities of the reagents on the left side. Now consider the two possible directions for the start of a reaction based on whatever conditions are given for the system.

Scenario 1. The given conditions are such that  $Q < K$ .

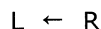
$Q$  is too small relative to  $K$ , so the exergonic direction is to increase  $Q$ . Since  $Q$  is too small, then the  $R/L$  ratio is also too small. The system must go forward, from left to right, in order to reach equilibrium.



Going in the forward direction increases the amounts of reagents on the right side of the equation and decrease the amounts on the left, and together this will increase the ratio  $R/L$ . Thus, FOR ANY SYSTEM WITH  $Q < K$ , THE FORWARD REACTION IS THE EXERGONIC DIRECTION since this increases  $Q$  in the direction of  $K$ .

Scenario 2. The given conditions are such that  $Q > K$ .

$Q$  is too large relative to  $K$ , so the exergonic direction is to decrease  $Q$ . Since  $Q$  is too large, then the  $R/L$  ratio is too large. The system must go reverse, from right to left.



This direction will decrease the rights and increase the lefts, and together this will decrease the R/L ratio. Thus, FOR ANY SYSTEM WITH  $Q > K$ , THE REVERSE REACTION IS THE EXERGONIC DIRECTION since this decreases  $Q$  in the direction of  $K$ .

These new  $Q$  vs.  $K$  relationships will come in handy. Keep them in mind.

### 51.2 More $\Delta G^\circ$ and $K$

We now look at some specific examples of reactions and their values for  $K$ . We did some examples in Chapter 47, but we are increasing our emphasis on  $K$  and the magnitude of  $K$ . As our emphasis changes, it is useful to keep in mind the fundamentals behind  $K$ . Let's take a look at how big this picture has become.

We start with the exponential form of the relationship between  $K$  and  $\Delta G^\circ$ .

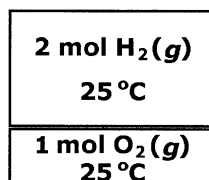
$$K = e^{-\Delta G^\circ/RT}$$

Remember that  $\Delta G^\circ$  derives from  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

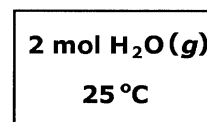
Ultimately,  $\Delta H^\circ$  and  $\Delta S^\circ$  give us the value for  $K$  at some  $T$ . Now recall the origins of  $\Delta H^\circ$  and  $\Delta S^\circ$ . We first introduced enthalpy in Chapter 18. Back then, we mentioned some of the factors which affect enthalpy using the example of the combustion of hydrogen.

“



**INITIAL**

The initial package has some total assets of energy as a result of having two moles of H<sub>2</sub> and one mole of O<sub>2</sub>, along with the energies of those molecules, and due to the fact that those molecules are gas phase (as opposed to some other phase), and due to the fact that they are all at 25 °C. Add up all such factors and you get the total enthalpy of the starting package, which we designate  $H_{\text{initial}}$ .



**FINAL**

This final package has some total assets of energy due to the fact that two moles of H<sub>2</sub>O are present along with the energies of those molecules, and due to the fact that those molecules are gas phase (as opposed to another phase), and due to the fact that they are at 25 °C. Add up all such factors and you get the total enthalpy of this package, which we designate  $H_{\text{final}}$ .

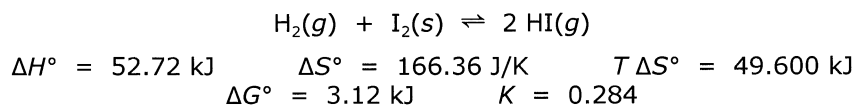
Notice that I threw in the bit about the energies of the molecules themselves. This energy primarily arises from the fact that different molecules have different bonds with different energies. During a reaction, some bonds are broken and new ones are made. That's a big part of the total energy of a chemical reaction, although other factors can also contribute. We'll see more about these bond energies in Chapter 25 and in Chapter 27. ”

Note the brief mention way back then of the importance of bond energies and phases on the energy (enthalpy) of a reaction. Since then, we have expanded those notions substantially. For many reactions, bond energies are the biggest factor for the change in enthalpy. Ionic bond energies were discussed in Section 25.2 and covalent bond energies in Section 25.4. We developed this further in Section 27.2 and demonstrated a method for estimating  $\Delta H$  for a gas phase reaction based only on average bond energies. In addition to bond energies, phases can also be important to a reaction's  $\Delta H^\circ$ . We saw the impact of phase on enthalpy in Chapter 34 and we connected this to intermolecular forces. In general, for reaction enthalpies of several hundred kJ or more, bond energies are likely the dominant factor. On the other hand, bond energies can also offset each other in a reaction, giving reaction enthalpies less than a hundred or so kJ; in these cases, the effect of the IFs of the phases can be comparable or even exceed the effects of bond energies. Beyond bond energies and IFs, other factors can also come into play. Redox can also have a big impact on the value  $\Delta H^\circ$ . We haven't done much with that yet, but we will work extensively with redox starting in Chapter 61. All of these things combine to give  $\Delta H^\circ$ 's contribution to the value of  $\Delta G^\circ$  and hence to  $K$ .

And then there's  $\Delta S^\circ$ . Entropy's contribution to  $K$  includes the entropy of the compounds themselves which are involved in the reaction. These aspects were described beginning in Chapter 44. Entropy's contribution to  $K$  also includes the phases of the various compounds. We had talked of this qualitatively starting in Chapter 34 and quantitatively starting in Chapter 44. In fact, one of the biggest factors for  $\Delta S^\circ$  for any reaction is whether the number of gas phase components changes during the reaction. All of these factors combine to give  $\Delta S^\circ$ 's contribution to the value of  $\Delta G^\circ$  and hence to  $K$ .

Now let's apply these fundamentals to four Cases at 25.00 °C.

Case A.



$\Delta H^\circ$  is fairly modest at only 52.72 kJ. The bond changes for this reaction involve breaking H–H and I–I single bonds and forming two H–I single bonds. The total bond energies left and right are pretty even for this reaction, so bond energies balance out somewhat. (See the values in Section 25.4.) The biggest contribution to  $\Delta H^\circ$  is actually getting  $\text{I}_2$  into gas phase with everything else. Since  $\text{I}_2$  starts out as solid, then its IFs are a considerable part of the total change in enthalpy for this reaction. Combining the effects of the bond energies and the IFs, we get the endothermic result for  $\Delta H^\circ$  of 52.72 kJ. For entropy,  $\Delta S^\circ$  is substantially positive, as to be expected for a reaction which produces more gases than it uses. Notice that enthalpy and entropy oppose each other, 52.72 kJ for  $\Delta H^\circ$  and 49.600 kJ for  $T \Delta S^\circ$ , but these values are close. The result is that  $\Delta G^\circ$  is very small at only 3.12 kJ. The thermodynamics tell us that neither side is greatly favored at standard conditions. We also see this by  $K = 0.284$ ; since this is the R/L ratio at equilibrium, there will be a significant amount on both the right and left sides of the equation at equilibrium.

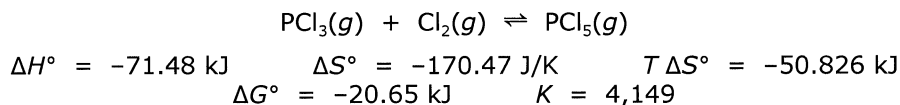
$$K = \frac{P(\text{HI})^2}{P(\text{H}_2)} = 0.284$$

If you start the reaction with both gases at 1.000 atm (and some amount of  $\text{I}_2(\text{s})$ ), then  $Q = 1.000$  which puts  $Q$  greater than  $K$ . Since  $Q$  is too large, the exergonic direction is reverse,  $\text{L} \leftarrow \text{R}$ . The net change is HI would form more  $\text{H}_2$  and  $\text{I}_2$ . At the point of equilibrium, you end up at

$$P(\text{H}_2) = 1.207 \text{ atm} \quad P(\text{HI}) = 0.586 \text{ atm}$$

along with more  $\text{I}_2(\text{s})$ . Notice that there are significant amounts of reagents on both sides of the equation when the process is done. In the next Chapter, you will see how to calculate such amounts for equilibrium.

Case B.



The bond energies for this reaction involve breaking a Cl–Cl single bond and making two PCl bonds, and this is the dominant effect for  $\Delta H^\circ$ . ( $\text{PCl}_5$  has expanded valence so the PCl bond energy values in Section 25.4 cannot be used as a comparison.) Entropy goes downhill, primarily due to losing a mole of gas overall. We end with a negative and modest  $\Delta G^\circ = -20.65 \text{ kJ}$  and a  $K$  in the thousands. With such a  $K$  value, the right side will dominate the system at equilibrium.

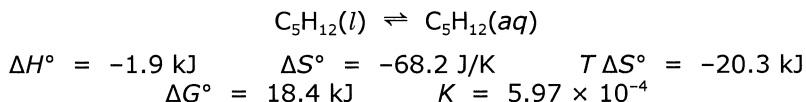
$$K = \frac{P(\text{PCl}_5)}{P(\text{PCl}_3) P(\text{Cl}_2)} = 4,149$$

If you start the reaction with all reagents at 1.000 atm each, then  $Q = 1.000$  and that is less than  $K$ .  $Q$  is too small and the exergonic direction is forward,  $\text{L} \rightarrow \text{R}$ . The net change is  $\text{PCl}_3$  and  $\text{Cl}_2$  would form more  $\text{PCl}_5$ , and you would end up at

$$P(\text{PCl}_3) = 0.022 \text{ atm} \quad P(\text{Cl}_2) = 0.022 \text{ atm} \quad P(\text{PCl}_5) = 1.978 \text{ atm}$$

when it reaches equilibrium. Notice that the amounts of  $\text{PCl}_3$  and  $\text{Cl}_2$  which remain are so little.

Case C.



This Case is different from the prior two because it only involves solubility and there is no chemical change involved. We had looked at these numbers back in Section 47.2 but now look at what's behind them. The  $\Delta H^\circ$  is primarily a result of IFs, none of which are impressive (Sections 37.6 and 39.3), leading to a  $\Delta H^\circ$  near zero. It is entropy which now dominates the  $\Delta G^\circ$ , and the substantial decrease in entropy is due to putting a hydrocarbon into water (Section 40.1). The  $\Delta G^\circ$  is modest but positive, sending  $K$  down into the thousandths range.

$$K = [\text{C}_5\text{H}_{12}(\text{aq})] = 5.97 \times 10^{-4}$$

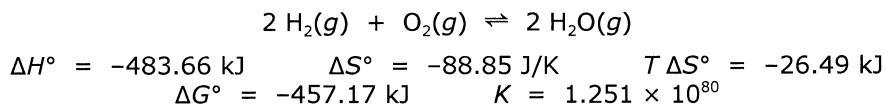
If you start the process with  $[\text{C}_5\text{H}_{12}(\text{aq})] = 1.000 \text{ M}$  (and some amount of  $\text{C}_5\text{H}_{12}(\text{l})$ ), then  $Q = 1.000$  and that is greater than  $K$ ;  $Q$  is too large and the exergonic direction is reverse,  $\text{L} \leftarrow \text{R}$ . The net change would be for some  $\text{C}_5\text{H}_{12}$  to leave the aqueous phase and form more of the liquid phase. This net change will continue until

$$[\text{C}_5\text{H}_{12}(\text{aq})] = 5.97 \times 10^{-4}$$

when it reaches equilibrium.

The three Cases so far have had moderate values for  $\Delta G^\circ$ . Although moderate,  $\pm 20 \text{ kJ}$  for  $\Delta G^\circ$  gets  $K$  into the thousands and thousandths range. Now let's go extreme.

Case D.



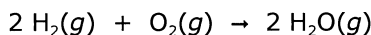
This ties back to the enthalpy illustration from Chapter 18 as repeated earlier in this Section, but now with all of the thermodynamic parameters. As noted,  $\Delta H^\circ$  is overwhelmingly due to bond energies. The drop in entropy is mostly due to loss of a mole of gas; this doesn't matter much to  $\Delta G^\circ$ , however, because  $T \Delta S^\circ$  is overshadowed by the very large  $\Delta H^\circ$ . With  $\Delta G^\circ$  in the negative hundreds,  $K$  is now astronomically huge.

$$K = \frac{P(\text{H}_2\text{O})^2}{P(\text{H}_2)^2 P(\text{O}_2)} = 1.251 \times 10^{80}$$

If you start the reaction with 1.000 atm of  $\text{H}_2$ , 0.500 atm of  $\text{O}_2$  and 1.000 atm of  $\text{H}_2\text{O}$ , then  $Q = 2.00$  and that is far less than  $K$ .  $Q$  is too small, and the exergonic direction is forward,  $\text{L} \rightarrow \text{R}$ . The net change is more combustion of  $\text{H}_2$  with  $\text{O}_2$  to form more  $\text{H}_2\text{O}$ . At equilibrium, you would end up with

$$P(\text{H}_2) = 3.999 \times 10^{-27} \text{ atm} \quad P(\text{O}_2) = 1.999 \times 10^{-27} \text{ atm} \quad P(\text{H}_2\text{O}) = 2.000 \text{ atm}$$

which basically means that only water remains. Although we can calculate these numbers, the amounts for  $\text{H}_2$  and  $\text{O}_2$  have no real significance. Although technically we can speak of equilibrium, on a practical basis the reaction goes all the way to the right. It would be fair to use a full single arrow for this reaction.



In essence, this is not an equilibrium process and there is no significant opposing process.

This ends the four Cases. Time to summarize and to emphasize.

As we head more and more into equilibrium, especially calculations involving equilibrium, it is easy to lose sight of what is all behind this. Bond energies are a big part, but even they can balance out in some cases. IFs can be significant to  $\Delta H^\circ$  (especially when ion-dipole is involved although that was not shown in the Cases here). If  $\Delta H^\circ$  is large, it will typically dominate over  $\Delta S^\circ$  for the relative impact on  $\Delta G^\circ$  but, when  $\Delta H^\circ$  is more modest, then  $\Delta S^\circ$  can be the more important contributor.

Note the range of  $K$  values in these Cases. The value of  $K$  is very sensitive to the value of  $\Delta G^\circ$  due to their exponential relationship.

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

Here is a table of sample  $K$  values based on a given  $\Delta G^\circ$  at 25.00 °C.

$\Delta G^\circ$ (kJ)	0.0	-5.0	-10.	-20.	-50.	-100.	-500.
$K$	1.0	7.5	56	3200	$5.8 \times 10^8$	$3.31 \times 10^{17}$	$3.99 \times 10^{87}$
$\Delta G^\circ$ (kJ)	0.0	5.0	10.	20.	50.	100.	500.
$K$	1.0	0.13	0.018	$3.1 \times 10^{-4}$	$1.7 \times 10^{-9}$	$3.02 \times 10^{-18}$	$2.51 \times 10^{-88}$

Check out the magnitude of the  $K$  values. These vary immensely even though  $\Delta G^\circ$  is only changing by tens or hundreds of kJs. Keep in mind that  $K$  is the R/L ratio when the reaction is "done". Reactions with small negative or small positive  $\Delta G^\circ$  will have  $K$  values in the range of  $10^2 - 10^{-2}$ , which can leave considerable amounts on the left and right sides of the equation when the reaction is done. Reactions with moderate but more negative  $\Delta G^\circ$  will have larger values of  $K > 10^2$ , and the amounts of reagents on the right side of the equation will dominate over the amounts on the left side of the equation at equilibrium. On the other hand, for reactions with moderate but more positive  $\Delta G^\circ$ , the smaller value of  $K < 10^{-2}$  will leave more amounts on the left side of the equation than on the right. As  $\Delta G^\circ$  gets more extreme, negative or positive,  $K$  becomes hugely large or vanishingly small. A reaction with  $\Delta G^\circ$  of negative several hundred kJ's will be overwhelmingly to the right at completion, with no significant sense of equilibrium. A reaction with  $\Delta G^\circ$  of positive several hundred kJ's will be overwhelmingly to the left, also with no significant sense of equilibrium. Small to moderate changes in  $\Delta G^\circ$  can have a very big effect on  $K$ .

As we speak of the amounts on the left or right side of an equation, you must keep in mind that these amounts refer to activities. As such, the amounts only apply for gases and solutes. Solids and liquids remain unity activity throughout. Although they will not affect  $K$ , the actual amounts of solids and liquids do change as a result of the usual stoichiometry considerations. Besides, in order to have equilibrium, in order to have the forward and the reverse processes operate at the same speed, then all reagents which are present in the equation must be present in the system. That includes some actual amount of solids and liquids.

We close here on the factors behind  $K$  and we will now enter more into the math side of equilibrium and the calculations which can ensue. Let me make one more brief point before departing for that entrance. I've already said several times going back to Chapter 47 that  $K$  is a constant as long as temperature is a constant. As  $T$  changes, then so does  $\Delta G^\circ$  due to its connection to  $\Delta H^\circ - T \Delta S^\circ$ . In addition, the equation for  $K$  also has a  $T$  in it.

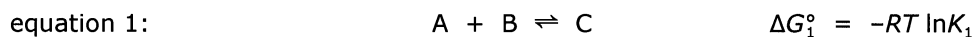
$$K = e^{-\Delta G^\circ/RT}$$

Thus, as  $T$  changes,  $K$  will change. We're going to look at this a bit more in Chapter 53, so we won't dwell on it for now. Let me just say that you may see different  $K$  values for the same reaction in different problems. That's OK, since different temperatures will be involved.

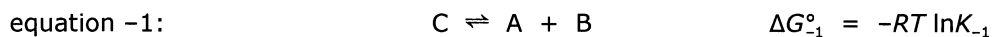
### 51.3 Three relationships for $K$ and $Q$

As we have seen since Chapter 19, the additivity of reactions leads to the additivity of the thermodynamic parameters of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ , all of which is a consequence of the conservation of mass-energy. We have also seen that reversing an equation negates the signs for these parameters. Ultimately,  $\Delta G^\circ$  rules all reactions, but its exponential/logarithmic connection to  $K$  changes the math of the analogous relationships for  $K$ . Since  $K$  is just one example of reaction quotient  $Q$ , then  $Q$  is likewise affected. Let's look at these relationships.

For our discussion here, we will only deal with generic equations so we can focus on the relationships themselves and not worry about compounds and phases right now. Consider a first equation, simply labeled equation 1, along with its free energy and  $K$ .



Now reverse the equation, which will be labeled equation -1.



Since equation -1 is simply the reverse of equation 1, then their  $\Delta G^\circ$ 's are simply the negative of each other

$$\begin{aligned} -\Delta G_{-1}^\circ &= \Delta G_1^\circ \\ +RT \ln K_{-1} &= -RT \ln K_1 \\ \ln K_{-1} &= -\ln K_1 = \ln(1/K_1) \end{aligned}$$

which means

$$K_{-1} = 1/K_1$$

and that is our final result: when you reverse an equation, you invert  $K$ . This is the FIRST RELATIONSHIP:

When you reverse an equation, you negate  $\Delta G^\circ$  but you invert  $K$  (and  $Q$ ).

We can also show this by spelling out the  $K$  or  $Q$  expressions for equations 1 and  $-1$ . For illustration purposes, we shall simply assume A, B, and C are solutes. For equations 1 and  $-1$  we can write

$$Q_1 = \frac{[C]}{[A][B]} \quad Q_{-1} = \frac{[A][B]}{[C]}$$

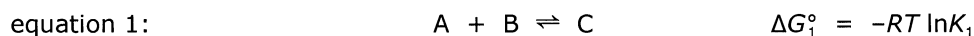
and from this you can see their inverse relationship.

If you look back upstairs at the table of sample  $\Delta G^\circ$  and  $K$  values, you can also see this relationship with those numbers. The table shows  $\pm\Delta G^\circ$  values in the same column. Pick a column and compare the  $\pm\Delta G^\circ$  values: the values of their  $K$ 's are inverted. For example:

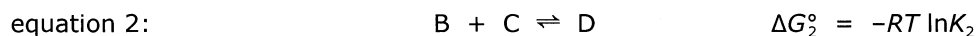
For  $\Delta G^\circ = -5.0$  kJ, the  $K$  is 7.5.

For  $\Delta G^\circ = +5.0$  kJ, the  $K$  is 0.13 and that is  $1/7.5$ .

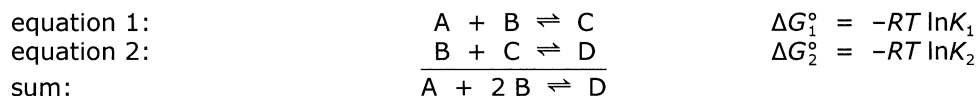
The next relationship deals with the additivity of equations. For that, we keep equation 1 above



and we bring in another equation, equation 2.



Now let's add equations 1 and 2.



Directly for the sum, we can write

$$\Delta G_{\text{sum}}^\circ = -RT \ln K_{\text{sum}}$$

and, since free energies are additive,

$$\Delta G_{\text{sum}}^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

then

$$\begin{aligned} -RT \ln K_{\text{sum}} &= (-RT \ln K_1) + (-RT \ln K_2) \\ \ln K_{\text{sum}} &= \ln K_1 + \ln K_2 = \ln(K_1 \times K_2) \end{aligned}$$

which leads to

$$K_{\text{sum}} = K_1 \times K_2$$

for the final result. This says that, when you add equations, you multiply their  $K$ 's to get the new  $K$  for the sum equation. This is the **SECOND RELATIONSHIP**:

When you add equations, you add their  $\Delta G^\circ$ 's but you multiply their  $K$ 's (and  $Q$ 's).

This point can also be seen by writing out the  $K$  or  $Q$  expressions for the respective equations

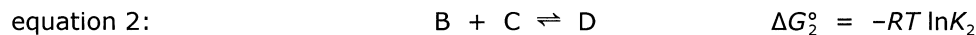
$$Q_1 = \frac{[C]}{[A][B]} \quad Q_2 = \frac{[D]}{[B][C]} \quad Q_{\text{sum}} = \frac{[D]}{[A][B]^2}$$

and showing that

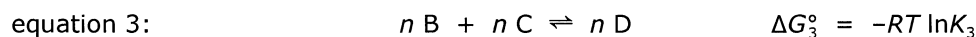
$$Q_1 \times Q_2 = \frac{[C]}{[A][B]} \times \frac{[D]}{[B][C]} = \frac{[D]}{[A][B]^2} = Q_{\text{sum}}$$

which brings us to the same conclusion.

For our final Relationship, we shall consider what happens to  $K$  when an equation is multiplied. We'll use equation 2 here



but now multiply the equation by some value  $n$ ; we'll label this equation 3.



When you multiply an equation, you multiply its  $\Delta G^\circ$ . Here, that means

$$\Delta G_3^\circ = n \Delta G_2^\circ$$

so

$$-RT \ln K_3 = n (-RT \ln K_2)$$

or

$$\ln K_3 = n \ln K_2 = \ln(K_2^n)$$

which leads to

$$K_3 = K_2^n$$

for the final result. When you multiply an equation by some value  $n$ , then its  $K$  is raised to the  $n$ th power. This is the THIRD RELATIONSHIP:

When you multiply an equation by  $n$ , you multiply  $\Delta G^\circ$  by  $n$  but you raise  $K$  (and  $Q$ ) to the  $n$ th power. Again, we can see this in the  $K$  or  $Q$  expressions

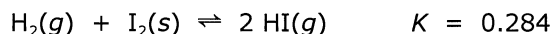
$$Q_2 = \frac{[D]}{[B][C]} \quad Q_3 = \frac{[D]^n}{[B]^n [C]^n}$$

which leads to the same result.

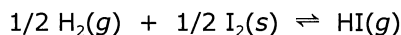
$$Q_3 = Q_2^n$$

This concludes the Three Relationships.

Why are these important? Well, they can help when we need to manipulate equations. We can use these relationships for  $K$  without having to go through  $\Delta G^\circ$  each time. As an example, consider the reaction for prior Case A.



What if you want  $K$  for the formation equation of  $\text{HI}(g)$ ? The formation equation of  $\text{HI}(g)$  is simply one-half of the above equation.



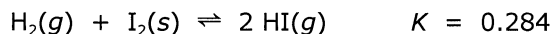
According to the Third Relationship,  $K$  for this equation is the original  $K$  to the one-half power.

$$\text{new } K = 0.284^{1/2} = 0.533$$

That was a pretty easy way to get the new  $K$ . Let's get a bit more complicated. What if you want  $K$  for the following equation?



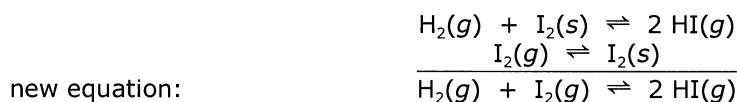
Note that  $\text{I}_2$  is now ( $g$ ). Assume you are again given the equation from Case A



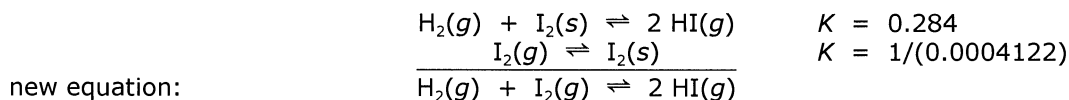
and you are also given the sublimation  $K$  for  $\text{I}_2(s)$ .



You can construct the new equation by additivity, except you have to reverse the sublimation equation for  $\text{I}_2(s)$  (which means it is now the deposition equation).



Now bring in the  $K$  values. For the deposition equilibrium, according to the First Relationship, you need to invert the  $K$  for sublimation.



Now, according to the Second Relationship, multiply these  $K$ 's to get the new  $K$ .



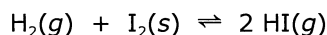
$$\text{new } K = 0.284 \times 1/(0.0004122) = 689$$

That's it.

### 51.4 General examples

We now start into various types of calculations which involve  $K$ . There are several uses for these. If we know a system is at equilibrium and if we can measure the amounts of all reagents present, then we can calculate  $K$ ; this also provides a means to determine  $\Delta G^\circ$ . Or, if we know  $K$  and if we can measure the amounts of some of the reagents, then we can calculate the amount of another reagent. Or, if we start with some given amounts of reagents and then let the system go to equilibrium, then we can calculate in advance where that system should end. Or, etc. There are quite a number of variations on these themes.

**Example 1.** Consider the following equilibrium at 298 K.



There are two Parts to this Example.

Part A. During one run of the system, the following amounts were measured at equilibrium.

$$0.0689 \text{ atm H}_2 \qquad 0.00691 \text{ mol I}_2 \qquad 0.140 \text{ atm HI}$$

From these amounts, calculate  $K$  at this temperature.

Part B. During another run of the system, the following amounts were measured.

$$0.0418 \text{ atm H}_2 \qquad 0.00771 \text{ mol I}_2 \qquad 0.132 \text{ atm HI}$$

Is the system at equilibrium? If not, which direction is exergonic?

For Part A, you are told the system is at equilibrium and you are given the amounts at equilibrium; you are asked for the value of  $K$ . We have this answer from Case A as shown earlier, but let's go ahead with the calculation. This is a simple plug-in to the  $K$  expression.

$$K = \frac{P(\text{HI})^2}{P(\text{H}_2)}$$

Although you are given an amount for  $\text{I}_2$ , you will not need it because  $\text{I}_2$  is solid phase and therefore unity activity. Plug in the activities for the gases.

$$K = \frac{(0.140)^2}{0.0689}$$

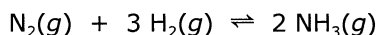
Punch it out and round it off and you get 0.284.

Part B. In this Part, you don't know if the system is at equilibrium. Since you don't know if this is equilibrium, we can solve for  $Q$  and see how that compares to  $K$ .

$$Q = \frac{P(\text{HI})^2}{P(\text{H}_2)} = \frac{(0.132)^2}{0.0418} = 0.417$$

$Q$  does not equal  $K$  so the system is not at equilibrium.  $Q > K$  so the R/L ratio is too high and the exergonic direction is reverse. The system would go in the reverse direction to reach equilibrium.

**Example 2.** Consider the following equilibrium in a container at 400. K and a gas volume of 86.1 L.



$K = 36.6$  at this temperature. Upon reaching equilibrium during one run, the pressure of nitrogen was found to be 0.217 atm and the pressure of ammonia was found to be 0.261 atm. Find the pressure of hydrogen and the total pressure under these conditions.

OK, the system is given to be at equilibrium and the value of  $K$  is provided. Pressures for two gases are given and you are asked for the pressure of the third gas and the total pressure in the system. You need a  $K$  expression.

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

Plug in what you have.

$$36.6 = \frac{(0.261)^2}{(0.217) P(\text{H}_2)^3}$$

Re-arrange and solve.

$$P(\text{H}_2) = \left( \frac{(0.261)^2}{(0.217)(36.6)} \right)^{1/3} = 0.205$$

This is an activity which relates to atm, so the answer for the pressure of  $\text{H}_2$  is 0.205 atm. Finally, as with any gas mixture, the total pressure is the sum of all individual pressures.

$$P_{\text{total}} = 0.217 \text{ atm} + 0.261 \text{ atm} + 0.205 \text{ atm} = 0.683 \text{ atm}$$

That's it.

These two Examples so far have dealt with gases and pressures only. We will also be doing a lot with solutes and concentrations. Furthermore, you can get into moles and grams if the problem so requests, and those will follow the usual relationships. As an illustration, let's take Example 2 one step further: how many grams of  $\text{H}_2$  are present at equilibrium?

That's no big deal: it just takes  $PV=nRT$ .  $V$  and  $T$  were provided information and you just calculated  $P$ .  $PV/nRT$  will get you  $n$ . Then bring in molar mass. When you do all of that, you should get 1.08 g. Be sure you can do so.

These problems are among the easiest types of calculations involving equilibrium, since they only involve a calculation using a given set of conditions. You plug your given conditions directly into  $K$  or  $Q$  and solve for whatever. A different type of problem begins with some set of initial conditions which then change as the reaction proceeds. Thus, the final conditions are changed from the initial conditions, and you need to solve for those. These can get into all sorts of variations, although even these are still fundamentally an equilibrium problem.

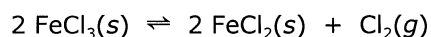
We start into those in the next Chapter.

## Problems

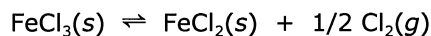
- True or false.
  - For any endergonic process,  $Q$  is less than  $K$ .
  - If  $Q > K$ , then  $\Delta G$  is positive.
  - When  $Q = K$ , the forward rate of the reaction and the reverse rate of the reaction are equal.
  - For any process, as  $\Delta G$  goes to zero, then  $Q$  goes to  $K$ .
  - A reaction with  $\Delta G^\circ = 400 \text{ kJ}$  will lie completely to the right upon completion.
- True or false.
  - Equilibria are dynamic.
  - If  $Q > K$ , then the exergonic direction is the reverse direction.
  - Small changes in  $\Delta G^\circ$  can give large changes in  $K$ .
  - When you double a chemical equation, you square its  $K$  value.
  - If  $Q < K$ , then the system can go to the right in order to reach equilibrium.
- Consider the following balanced equation and  $K$ .



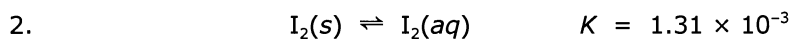
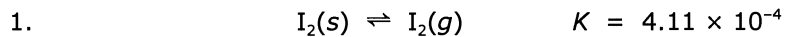
- What is  $K$  for the following equation?



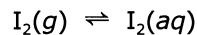
b. What is  $K$  for the following equation?



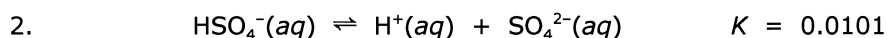
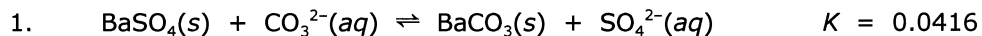
4. Consider the following equilibria.



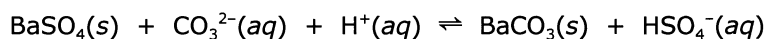
What is  $K$  for the following?



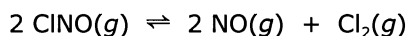
5. Consider the following equilibria.



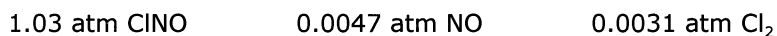
What is  $K$  for the following?



6. Consider the following equilibrium system.

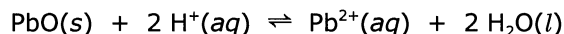


The following conditions were measured at equilibrium.



What is the value for  $K$ ?

7. Consider the following equilibrium system.



The following conditions were measured at equilibrium.



What is the value for  $K$ ?