

## Chapter 46

## CAN IT HAPPEN? Part 3

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We continue with various quantitative aspects of free energy.

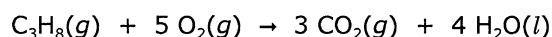
## 46.1 Stoichiometry

As mentioned, the four Important Aspects from Chapter 19 apply to all of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ . Consider Important Aspect 3 from Chapter 19; that led to stoichiometry problems for  $\Delta H^\circ$  in Sections 19.4 and 19.5. You can do stoichiometry with  $\Delta G^\circ$  which we will illustrate with a single example. The calculations are the same as those seen in Chapter 19 for  $\Delta H^\circ$ . In fact, we shall use a variation on the propane Example 4 from that Chapter.

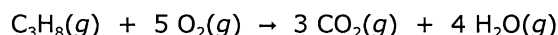
“ How many kJ's can you get from the combustion of 1.000 g propane at standard conditions? ”

Back then, the kJ's were for the change in enthalpy. Now, we do it for the change in free energy.

We need an equation. In Chapter 19 we chose



but, in the last Chapter, we chose the version



which has  $\text{H}_2\text{O}$  as gas instead of liquid. For this second version, we calculated  $\Delta G_c^\circ = -2,073.19$  kJ. Let's work with this one since we have the  $\Delta G_c^\circ$  already. That  $\Delta G_c^\circ$  is for the reaction as written. Now we want the change in free energy for combustion of 1.000 g propane.

$$1.000 \text{ g C}_3\text{H}_8 \times \frac{\text{mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-2,073.19 \text{ kJ}}{\text{mol C}_3\text{H}_8} = -47.02 \text{ kJ}$$

That's just like the stoichiometry setup in Chapter 19 and that's all there is to it.

## 46.2 Temperature effects

From the last Chapter:

“ In all of these, keep in mind that it's always  $\Delta H_{\text{sys}}$  and  $T \Delta S_{\text{sys}}$ . Temperature is part of this picture. Raising  $T$  will always increase entropy's impact on  $\Delta G_{\text{sys}}$ ; lowering  $T$  will always decrease entropy's impact on  $\Delta G_{\text{sys}}$ . For Variations 3 and 4, even changing the temperature can change the final sign for  $\Delta G_{\text{sys}}$ . You'll see this, but it will wait until later after we get into some numbers. ”

Later is now.

I will preface this by noting that Variation 1 is always exergonic and temperature cannot change that. Variation 2 is always endergonic and temperature cannot change that. On the other hand, Variations 3 and 4 have enthalpy and entropy in opposition to each other for the sign of  $\Delta G^\circ$ . Increasing temperature will increase entropy's impact in that opposition.

Let's do an illustration. Consider some process



for which  $\Delta H^\circ = 12.0$  kJ and  $\Delta S^\circ = 35.0$  J/K. This process is endothermic but the system entropy increases. This is Variation 4.

$$\Delta G^\circ = \overset{(+)}{\Delta H^\circ} - T \overset{(+)}{\Delta S^\circ}$$

Enthalpy and entropy oppose each other.  $\Delta S^\circ$  is positive and favors exergonic; thus, increasing  $T$  will make  $\Delta G^\circ$  more negative (less positive), thereby enhancing spontaneity. Let's see it with numbers. Calculate  $\Delta G^\circ$  at 25.00 °C (298.15 K) and at 125.00 °C (398.15 K).

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

$$298.15 \text{ K: } \Delta G_{298.15}^\circ = 12.0 \text{ kJ} - (298.15 \text{ K})(35.0 \text{ J/K}) = 12.0 \text{ kJ} - 10.4 \text{ kJ} = 1.6 \text{ kJ}$$

$$398.15 \text{ K: } \Delta G_{398.15}^\circ = 12.0 \text{ kJ} - (398.15 \text{ K})(35.0 \text{ J/K}) = 12.0 \text{ kJ} - 13.9 \text{ kJ} = -1.9 \text{ kJ}$$

At 25.00 °C, the process is forbidden; at 125.00 °C, the process is allowed.

If you consider the reverse direction for this example, then  $\Delta H^\circ = -12.0$  kJ and  $\Delta S^\circ = -35.0$  J/K and this is Variation 3. The signs are the following.

$$\Delta G^\circ = \overset{(-)}{\Delta H^\circ} - T \overset{(-)}{\Delta S^\circ}$$

$\Delta S^\circ$  is negative and that favors endergonic. Increasing  $T$  makes  $\Delta G^\circ$  less negative (more positive), thus opposing spontaneity.

As can be seen, temperature can impact a reaction in terms of whether it's allowed or not. Putting it another way, temperature can determine the allowed direction of some reactions. For example, in the first process calculated above, the forward direction,  $A \rightarrow Z$ , is allowed at 125 °C but the reverse direction,  $A \leftarrow Z$ , is allowed at 25 °C. This is only possible for Variations 3 and 4 but not for Variation 1 (always exergonic) or Variation 2 (always endergonic). Even for Variations 3 and 4, it will not always be practical to change the direction of spontaneity if an extreme temperature is needed.

There's another important point to note. When the  $\Delta G^\circ$  of some process switches signs between two temperatures then, somewhere between those two temperatures,  $\Delta G^\circ$  goes through zero. That is the temperature of equilibrium at standard conditions. This  $T$  can be determined algebraically. Using the above example, set  $\Delta G^\circ =$  zero for equilibrium.

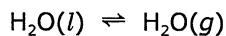
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = 12.0 \text{ kJ} - T (35.0 \text{ J/K}) = 0.0 \text{ kJ} \\ 12.0 \text{ kJ} &= T (35.0 \text{ J/K}) = T (0.0350 \text{ kJ/K}) \\ T &= 343 \text{ K}\end{aligned}$$

Thus, the system is at equilibrium at standard conditions at 343 K (70. °C).

We need to note a technicality here. We used numbers for  $\Delta H^\circ$  and  $\Delta S^\circ$  at different temperatures in these examples. In general, there is a slight variation of  $\Delta H^\circ$  and  $\Delta S^\circ$  with temperature, so those numbers themselves change with  $T$ . The variations are small and it is common practice to allow the use of  $\Delta H^\circ$  and  $\Delta S^\circ$  values over a modest range of temperatures for general work. We will adopt this practice, although sometimes I may throw in a different number for a different temperature. NOTE! The same practice does not apply for  $\Delta G^\circ$  because  $\Delta G^\circ$  expressly contains  $T$  within  $\Delta H^\circ - T \Delta S^\circ$ . Thus, you must calculate a different  $\Delta G^\circ$  for every different  $T$ .

Let's do another example. Calculate the nbp for water from the enthalpy and entropy of vaporization.

Huh? Normal boiling point? For water? OK, yes, you already know that nbp is 100.0 °C for water, but you can also calculate it from enthalpy and entropy. How? Well, what does nbp mean? As described in Chapter 35, it's the temperature for equilibrium for vaporization at a pressure of one atm. In other words, it's the temperature for equilibrium at standard conditions. Let's calculate that  $T$ . Start with an equation.



Since we seek  $T$  for equilibrium at standard conditions, we seek  $T$  for  $\Delta G_{\text{vap}}^\circ =$  zero. And for this, we will need to know  $\Delta H_{\text{vap}}^\circ$  and  $\Delta S_{\text{vap}}^\circ$ .

	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_2\text{O}(g)$
$\Delta H_f^\circ:$	-285.83 kJ		-241.83 kJ
$S^\circ:$	69.95 J/K		188.83 J/K

$$\begin{aligned}\Delta H_{\text{vap}}^\circ &= 1(-241.83 \text{ kJ}) - 1(-285.83 \text{ kJ}) = 44.00 \text{ kJ} \\ \Delta S_{\text{vap}}^\circ &= 1(188.83 \text{ J/K}) - 1(69.95 \text{ J/K}) = 118.88 \text{ J/K}\end{aligned}$$

Now put it together.

$$\Delta G_{\text{vap}}^\circ = \Delta H_{\text{vap}}^\circ - T \Delta S_{\text{vap}}^\circ = 44.00 \text{ kJ} - T (118.88 \text{ J/K})$$

Set  $\Delta G^\circ = 0.00$  kJ

$$0.00 \text{ kJ} = 44.00 \text{ kJ} - T (118.88 \text{ J/K})$$

and solve for  $T$ .

$$T = \frac{44.00 \text{ kJ}}{0.11888 \text{ kJ/K}} = 370.1 \text{ K}$$

OK, 370.1 K is not quite the real answer of 373.2 K, but the error is fairly small (<1%) and it arises from using values for  $\Delta H_{\text{vap}}^{\circ}$  and  $\Delta S_{\text{vap}}^{\circ}$  which technically are for 298.15 K.

Look at what we've done so far here. We can make a HUGE connection back to our early discussions on phase and phase change, beginning in Chapter 34. Chapter 35 talked further and more extensively about vaporization/condensation and the role of enthalpy and entropy.

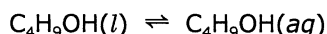
“ The above description is only one way of describing the balance of equilibrium. We can also describe the equilibrium as the balance between enthalpy (IFs, which favor liquid) and entropy (which favors gas). Neither wins overall, so neither the liquid phase nor the gas phase wins completely. Both phases are present and both phase changes continue to occur, but they are equally favored and they occur at the same speed. The system is in balance. ”

We are now putting numbers to the balance of enthalpy and entropy, and the final outcome is contained within free energy. The vaporization of water is Variation 4, and enthalpy and entropy oppose each other for the sign of  $\Delta G^{\circ}$ . We've also just calculated  $n_{\text{bp}}$  for the process. All of the qualitative aspects of those prior Chapters are now reflected in the change in free energy of the process. In fact, all phase changes for single compounds are either Variation 3 or Variation 4, in which enthalpy and entropy oppose each other for the sign of  $\Delta G$ .

Let's see another calculation, now dealing with a mixture.

.....  
**Example 1.** Calculate the temperature for equilibrium at standard conditions for dissolving 1-butanol,  $\text{C}_4\text{H}_9\text{OH}$ , into water.  
 .....

Start with an equation.



For this problem, standard conditions mean a concentration of one molar for  $\text{C}_4\text{H}_9\text{OH}(aq)$ . To simplify matters, I'll just tell you that  $\Delta H_{\text{soln}}^{\circ} = -9.23 \text{ kJ}$  and  $\Delta S_{\text{soln}}^{\circ}$  is in Chapter 44. Now, find  $T$  for  $\Delta G^{\circ} = \text{zero}$ .

Your answer is in kelvins as usual. If you want to check your answer, it's 88 °F. After you check your answer, note the connections to the prior discussions on solubility. Section 39.1:

“ The energy (enthalpy) issues are again tied up in intermolecular forces. The entropy issues are again tied up in options. In Chapters 34 - 38, the phases themselves were the outcome of the balance of enthalpy versus entropy. Now, for the determination of soluble/insoluble (and of miscible/immiscible), enthalpy and entropy may still oppose each other in some cases but, in other cases, enthalpy and entropy may both favor soluble or they may both favor insoluble. ”

The solubility of 1-butanol in water is Variation 3, and enthalpy and entropy oppose each other. (Solubility processes can fall under any of Variations 1 - 4.) We repeatedly cited 1-butanol as an example in Chapters 39 and 40 and now we see the numbers involved. These are important connections to make and there will be more opportunities for such connections in later Examples. The Grand Puzzle is still under construction and various interconnections continue to be made.

### 46.3 Standard conditions

So far, we've been holding to standard conditions although we have been varying  $T$ . Regardless of 25 °C or some other  $T$ , you need to understand what is meant by specifying standard conditions. Before doing that, let's summarize standard conditions as we are using them. These are still pretty much the same as those spelled out in Section 19.2, but some additions/variations have arisen.

Standard pressure = one atm (technically, one bar)

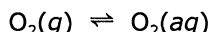
Standard concentration = one molar for aqueous solutes (technically, one molal, any solvent)

Standard temperature = undefined, but assumed to be exactly 25.00 °C unless told otherwise

While thermodynamic values for  $\Delta H_f$ ,  $S$  and  $\Delta G_f$  for any individual substance can vary with temperature, these can also vary with the conditions of pressure or concentration, but that will depend on the phase of the substance. For pure substances, the physical properties of gases are strongly dependent on pressure (as we had seen via  $PV=nRT$  and  $d$  back in Chapter 16) and these affect  $\Delta H_f$ ,  $S$  and  $\Delta G_f$ . As such, pressure needs to be a specified condition for gases. For a pure liquid and for a pure solid, however, pressure has very little effect on physical parameters. (At very high pressures, you will get effects but we will not consider those conditions here.) As such, we consider the values of thermodynamic properties of pure liquids and solids at any condition of pressure to equal the values at standard conditions. For a solute, the concentration of that solute will impact its values for  $\Delta H_f$ ,  $S$  and  $\Delta G_f$ , so concentration must be a specified condition for a solute.

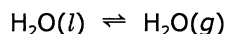
The thermodynamic requirement to specify a condition for a gas or a solute, but not for a liquid or a solid, will be extremely important in the next Section.

In the last Chapter we looked at  $O_2(g)$  dissolving into water.



We found that  $\Delta G_{\text{soln}}^\circ = 16.4 \text{ kJ}$  which means the process cannot happen by itself under the given conditions. Does this mean  $O_2(g)$  cannot dissolve in water at all? That would make a lot of fish very unhappy.

Consider again the evaporation of water at 25.00 °C.



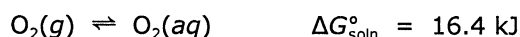
Using  $\Delta H_{\text{vap}}^\circ$  and  $\Delta S_{\text{vap}}^\circ$  from the illustration upstairs, you would find  $\Delta G_{\text{vap}}^\circ = 8.56 \text{ kJ}$ . That's endergonic. Evaporation of water cannot happen by itself under the given conditions. But water does evaporate at 25 °C. We know that from common experience. How can water evaporate at 25 °C if evaporation is endergonic at these conditions?

In both of these illustrations, the process is endergonic and cannot happen by itself under the given conditions. Whenever you see that little ° on a  $\Delta H$  or a  $\Delta S$  or a  $\Delta G$ , then the given conditions are standard conditions. Here, these two processes are endergonic at standard conditions. That's all that it says. **THAT DOESN'T MEAN THE PROCESSES ARE ENDERGONIC AT ALL CONDITIONS.** You must understand this distinction. And in order to understand this distinction, we need to elaborate on the meaning of standard conditions.

Every thermodynamic delta function is the difference between final and initial. It's also somewhat like a comparison. If we specify standard conditions, then we are comparing the final state at standard conditions to the initial state at standard conditions. In doing this comparison, we can consider all reagents to be present on both sides of the equation, with everything at standard conditions. From this point of standard conditions, the sign of  $\Delta G^\circ$  determines which direction is the allowed direction.

By the way, whenever we speak of the allowed direction, it is always for the allowed direction of net change. As a process or reaction occurs, both directions may be operating but they will not operate to the same extent (unless the system is in balance at equilibrium). The net change is the difference, and this is always in the direction of the negative  $\Delta G^\circ$ . This is very important and will be general for all conditions, so keep it in mind.

Let's re-examine the above processes in terms of everything at standard conditions. We will also specify mole amounts as given by the coefficients in the balanced equation for present illustration purposes.



We consider a container system which has an overhead gas space of one mol  $O_2(g)$  with  $P = \text{one atm}$  and a solution of one mol  $O_2(aq)$  with  $[O_2(aq)] = \text{one M}$ .



Starting the process from this point, the positive sign of  $\Delta G_{\text{soln}}^\circ$  says the forward process is endergonic; more dissolving cannot happen by itself. However, the reverse process is the allowed direction of net change: more  $O_2(aq)$  can escape to the gas phase and more  $O_2(g)$  can form. This can continue until the system hits equilibrium, at which point the system is in balance and there is no further net change. At

equilibrium, there will be less than one mol of  $O_2(aq)$  and  $[O_2(aq)]$  will be less than one M. There will also be more than one mol of  $O_2(g)$ .

Let's return to the vaporization of water.

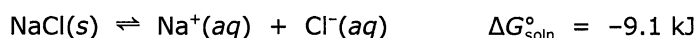


We consider a container system which has an overhead gas space containing one mol  $H_2O(g)$  with  $P =$  one atm and one mol of pure  $H_2O(l)$  in the bottom of the container.

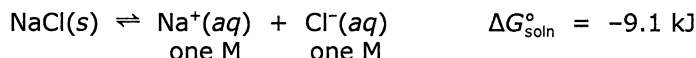


At these conditions, the sign of  $\Delta G_{\text{vap}}^{\circ}$  is positive and the forward process is endergonic; more vaporization cannot happen by itself. However, the reverse process, condensation, is allowed. Net change can happen in the reverse direction: this decreases  $P$  of  $H_2O(g)$  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 me bring in an illustration from Section 45.5.



We begin with one mol  $NaCl(s)$  in contact with a solution of one mol of dissolved  $NaCl(aq)$  at a concentration of one M for each dissociated ion.



The negative sign of  $\Delta G_{\text{soln}}^{\circ}$  says that even more can dissolve. Even that will eventually go to equilibrium; at equilibrium, there will be less than one mol of  $NaCl(s)$ , and both  $[Na^+(aq)]$  and  $[Cl^-(aq)]$  will be greater than one M.

As you can hopefully see from these examples, it is important to understand the conditions for the given  $\Delta G^{\circ}$ . The sign of  $\Delta G^{\circ}$  tells us the allowed direction for net change in a system when comparing all reactants at standard conditions to all products at standard conditions. Ultimately, however, we need to look at conditions other than standard. Thus, we need to generalize  $\Delta G$  to any set of conditions, standard or not.

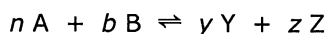
#### 46.4 General conditions

Whenever one or more components of the system are not at standard conditions, then we deal with the general  $\Delta G$  (without  $^{\circ}$ ). The connection which relates  $\Delta G$  to  $\Delta G^{\circ}$  is the following.

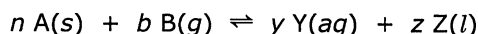
$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$R$  is the usual gas-constant-turned-physical-constant, in units of 8.314 J/(mol • K) (Chapter 17) or just 8.314 J/K without the mol term.  $T$  is still temperature.  $Q$  is new.

$Q$  is the reaction quotient. It is the ratio (quotient) of the given thermodynamic parameters of all components in the balanced equation. In this usage, the thermodynamic parameters are called activities,  $a$ . An activity for any item in the balanced equation is its actual, given condition relative to standard condition, but this can manifest in different ways depending on the phase of the item. Let's develop this using a generic equation as shown below; capital letters denote substances and lower case italic letters are coefficients.



(FYI. Since the activity is designated by 'a', I am using  $n$  for the coefficient of reactant A to avoid confusion.) Let's bring in phases for this illustration.



Now we'll see how this works out.

$Q$  is the ratio of the activities of all products over all reactants, all raised to powers equal to their coefficients in the balanced equation. An activity will be written as  $a(\ )$ , so  $Q$  takes the following form.

$$Q = \frac{a(Y)^y a(Z)^z}{a(A)^n a(B)^b}$$

Another way of saying this is simply "rights over lefts", R/L, meaning products (right side of equation) over reactants (left side of equation). Just remember that each activity is raised to its coefficient power. Standard conditions are the thermodynamic reference point for these calculations and all other conditions are relative to standard. That relative relationship is the activity. For example, for item A, we can write its activity as follows.

$$a(A) = \frac{\text{actual condition of A}}{\text{standard condition for A}}$$

The actual condition is whatever condition is given by the problem at hand. The standard condition is the same as summarized at the beginning of the last Section.

This may seem a bit complicated, but it actually breaks down very easily depending on the phases involved. Let's start with a solid as illustrated by compound A in our equation above. As noted in the last Section, the thermodynamic values of a solid do not vary with conditions (other than temperature) and the values at any condition can thus be taken as equal to the values at standard condition. This gives an activity ratio of one.

$$\text{Solids:} \quad a(A) = \frac{\text{actual}}{\text{standard}} = 1$$

Thus, all solid compounds are entered into  $Q$  as exactly one, without units. I shall refer to this as unity condition or unity activity. All solids have unity activity (unity condition). Since  $a(A)^n = 1^n = 1$ , then the coefficient of A in the balanced equation won't matter either. In the  $Q$  expression itself, we can leave out all solids because their activities equal one.

$$Q = \frac{a(Y)^y a(Z)^z}{a(A)^n a(B)^b} = \frac{a(Y)^y a(Z)^z}{(1^n) a(B)^b} = \frac{a(Y)^y a(Z)^z}{a(B)^b}$$

Now consider a liquid phase component in the balanced equation, represented above by product Z. Thermodynamic conditions for liquids are similar as for solids: thus, any pure liquid will also constitute a unity condition.

$$\text{Liquids:} \quad a(Z) = \frac{\text{actual}}{\text{standard}} = 1$$

Since  $a(Z)^z = 1^z = 1$ , we can leave that activity out of  $Q$  also.

$$Q = \frac{a(Y)^y a(Z)^z}{a(B)^b} = \frac{a(Y)^y (1^z)}{a(B)^b} = \frac{a(Y)^y}{a(B)^b}$$

Let's consider a gas phase. Standard conditions for gases do have a condition stipulated by pressure, so that changes things. We must take into account the actual pressure for each gas phase component in a balanced equation. Furthermore, we take standard pressure to be one atm, so the actual condition must be entered relative to one atm. For our generic reaction, reactant B is gas phase.

$$\text{Gases:} \quad a(B) = \frac{\text{actual}}{\text{standard}} = \frac{\text{actual } P_B \text{ in atm}}{\text{one atm}}$$

Notice in this ratio that the atm units drop out. This is an essential feature of any activity for you to keep in mind. Activities have no units. They are ratios of actual to standard conditions, and all units cancel. Remember this. Although the activity has no units, we will continue to represent the activity of a gas by  $P$  but it will be understood to be a number of atm's without the atm unit.

Let's place this result into the  $Q$  expression.

$$Q = \frac{a(Y)^y}{a(B)^b} = \frac{a(Y)^y}{P_B^b} \quad (--- P \text{ is understood to be a number of atm's but is unitless.})$$

Finally, we look at a solute in the balanced equation, represented by product Y. We specify standard conditions for an aqueous solute to be a concentration of one M. We must take into account the actual

concentration for each solute. The treatment parallels the treatment for gases, but we deal with concentration instead of pressure.

$$\text{Solutes:} \quad a(Y) = \frac{\text{actual}}{\text{standard}} = \frac{\text{actual [Y] in M}}{\text{one M}}$$

The units cancel again. Thus, the activity of Y is the number for the molarity without the M unit. Take this into Q.

$$Q = \frac{a(Y)^y}{P_B^b} = \frac{[Y]^y}{P_B^b} \quad \begin{array}{l} \text{(-- [Y] is understood to be a number of M's but is unitless.)} \\ \text{(-- P is understood to be a number of atm's but is unitless.)} \end{array}$$

This is our final result for the reaction quotient for our generic equation.

This completes the four types of components which we consider for Q expressions. Let's summarize these.

- Solid and liquid components are at unity activity.
- Gas components enter into Q as a pressure in atm but without the atm unit.
- Solute components enter into Q as a concentration in M but without the M unit.

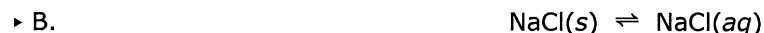
Here's an important result: since all activities are numbers without units, then Q itself is also just a number without units. Here's another important result: if all of the actual conditions are given to be equal to standard conditions, then all activities for all phases are equal to one and Q itself equals one.

OK, let's do some examples for setting up Q expressions for equations which were used earlier in this Chapter and in the last Chapter. Remember, a reaction quotient is rights over lefts, each involving an activity raised to a coefficient power.

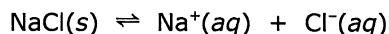


$\text{O}_2(g)$  is entered as a P without the atm unit.  $\text{O}_2(aq)$  is entered as a concentration without the M unit.

$$\Rightarrow \Rightarrow \Rightarrow \quad Q = \frac{[\text{O}_2(aq)]}{P(\text{O}_2(g))}$$



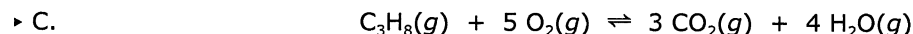
$\text{NaCl}(s)$  is unity condition. For  $\text{NaCl}(aq)$ , we hit a technicality. Although thermodynamic values for  $\text{NaCl}(aq)$  are equivalent to those for  $\text{Na}^+(aq) + \text{Cl}^-(aq)$  under full dissociation, this equivalence doesn't work for a Q. You ABSOLUTELY MUST present this as the fully dissociated ions. Rewrite the equation as such.



Now derive the Q expression.

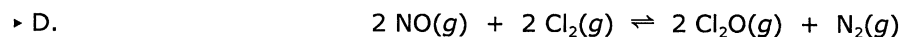
$$\Rightarrow \Rightarrow \Rightarrow \quad Q = \frac{[\text{Na}^+(aq)][\text{Cl}^-(aq)]}{1} = [\text{Na}^+(aq)][\text{Cl}^-(aq)]$$

If you did not dissociate the ions, you would get  $Q = [\text{NaCl}(aq)]$ , which is wrong. Remember this technicality when dealing with strong electrolytes, and be prepared to switch an equation into net ionic format if needed.



Everything is gas phase. Everything is entered as a pressure without the atm unit.

$$\Rightarrow \Rightarrow \Rightarrow \quad Q = \frac{P(\text{CO}_2)^3 P(\text{H}_2\text{O})^4}{P(\text{C}_3\text{H}_8) P(\text{O}_2)^5}$$



Your turn.

$$\Rightarrow \Rightarrow \Rightarrow \quad Q = \underline{\hspace{10em}}$$



$\text{H}_2\text{O}(l)$  is unity condition.

$$\Rightarrow \Rightarrow \Rightarrow \quad Q = P(\text{H}_2\text{O}(g))$$



$\text{C}_4\text{H}_9\text{OH}(l)$  is unity condition.

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

Hopefully this is catching on. We'll be doing more examples as we get into calculations with nonstandard conditions.

Notice in these examples that the final results for the  $Q$  expressions do not show any liquids or solids. Keep this in mind.

Alright, we've defined and assigned  $Q$ . Now we return to general  $\Delta G$ .

### 46.5 Getting into $Q$

Let's get our equation back.

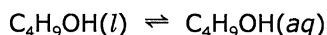
$$\Delta G = \Delta G^\circ + RT \ln Q$$

Now we're ready to proceed. This equation gives  $\Delta G$  for any set of conditions. Notably, that includes standard conditions: since  $Q$  equals one at standard conditions, then  $\ln Q$  equals zero and that term falls out. Thus, we still get  $\Delta G = \Delta G^\circ$  at standard conditions.

Now some nonstandard examples.

.....  
**Example 2.** You have a solution which contains 0.663 M  $\text{C}_4\text{H}_9\text{OH}(aq)$  at 25.00 °C. You add  $\text{C}_4\text{H}_9\text{OH}(l)$  to the system. What is  $\Delta G$  for dissolving under these conditions? Can any of the added  $\text{C}_4\text{H}_9\text{OH}(l)$  dissolve? For this process,  $\Delta G_{\text{soln}}^\circ = -0.17$  kJ.  
 .....

Write the equation.



As shown upstairs,  $Q = [\text{C}_4\text{H}_9\text{OH}(aq)]$ . The problem gives the actual  $[\text{C}_4\text{H}_9\text{OH}(aq)]$  as 0.663 M. That means  $Q = 0.663$ , with no units. Plug everything into  $\Delta G$ .

$$\Delta G = \Delta G^\circ + RT \ln Q = -0.17 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(0.663)$$

$$\Delta G = -0.17 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K})(-0.41098\dots)$$

$$\Delta G = -0.17 \text{ kJ} + (-1,020 \text{ J}) = -0.17 \text{ kJ} + (-1.02 \text{ kJ}) = -1.19 \text{ kJ}$$

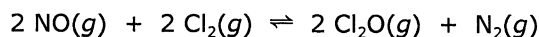
That's  $\Delta G$ . It's negative, so the process is allowed. Starting from the given conditions, more  $\text{C}_4\text{H}_9\text{OH}$  can dissolve, until equilibrium is reached.

TWO POINTS. First,  $\Delta G^\circ$  is typically in kJ and the  $RT$  term is in J. You must convert J into kJ. That was done in the last line of the equations above. Second, we have a new issue to worry about. This is our first logarithmic calculation. I warned you about these way back in Chapter 1. Let me tell you how we are going to handle sigfigs for this.

Most logarithms are natural (base  $e$ ) or common (base 10). Here we deal with  $\ln$ . We don't get into common log until Chapter 54. For sigfig purposes, I'm going to keep this real simple for now. For natural logs, we will just follow the multiplication/division rule. In the calculation above, you take  $\ln$  of 0.663, then multiply that by 8.314 and then by 298.15. Round that to three sigfigs (because 0.663 has the fewest with three) to get  $-1.02$  kJ. Finally, add the result to  $-0.17$ .

When we get into common log in Chapter 54, we'll get into rules for sigfigs for those. That's later, not now.

.....  
**Example 3.** Consider another reaction from previously.





The system starts with the following pressures for each component.

NO: 0.406 atm      Cl<sub>2</sub>: 0.389 atm      Cl<sub>2</sub>O: 0.00727 atm      N<sub>2</sub>: 0.0132 atm

Find  $\Delta G$  for these conditions. Under these conditions, in which direction can the reaction proceed?

.....

You calculated  $\Delta G^\circ$  at the end of the last Chapter and you set up  $Q$  for this reaction in the prior Section of this Chapter. Now plug everything in.

$$\Delta G = \Delta G^\circ + RT \ln Q = 20.96 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln \frac{(0.00727)^2 (0.0132)}{(0.406)^2 (0.389)^2}$$

$$\Delta G = 20.96 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(0.00027969\dots)$$

$$\Delta G = 20.96 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K})(-10.484\dots)$$

$$\Delta G = 20.96 \text{ kJ} + (-26.0 \text{ kJ}) = -5.0 \text{ kJ}$$

At these conditions, the reaction is exergonic although the reaction is endergonic at standard conditions. At the given conditions, the forward process can happen, until equilibrium is reached.

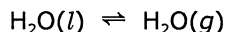
Next.

.....

**Example 4.** Let's evaporate some water at 25.00 °C. Or can we? Well, that depends. If a bucket of H<sub>2</sub>O(*l*) is placed into a room which has some humidity in the air with  $P(\text{H}_2\text{O}(g)) = 6.65$  Torr, can more liquid water evaporate from the bucket?

.....

Set it up.



From earlier in this Chapter (Section 3), we have  $\Delta G^\circ = 8.56$  kJ and we have  $Q = P(\text{H}_2\text{O}(g))$  (Section 4). Now plug everything in. Remember that a pressure in  $Q$  must be entered as an atm value; thus, you need to convert the given Torr to atm.

$$\Delta G = \Delta G^\circ + RT \ln Q = 8.56 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln \frac{6.65}{760}$$

$$\Delta G = 8.56 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(0.0087500\dots)$$

$$\Delta G = 8.56 \text{ kJ} + (8.314 \text{ J/K})(298.15 \text{ K})(-4.7387\dots)$$

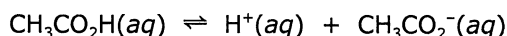
$$\Delta G = 8.56 \text{ kJ} + (-11.7 \text{ kJ}) = -3.1 \text{ kJ}$$

Exergonic. Yes, evaporation is allowed starting at the given condition, until equilibrium is reached. We can relate this to the discussion of vapor pressure and of EVP back in Chapter 35. In the list in Section 35.2, the EVP for water at 25 °C is given as 23.8 Torr. Here we started at 6.65 Torr, less than EVP. Thus, the condition for the H<sub>2</sub>O(*g*) in the air as given in this problem is unsaturated and that means more evaporation is possible.

OK, your turn.

.....

**Example 5.** Let's change things a bit and do something different: dissociation of a weak acid. Acetic acid was first introduced as a weak acid in Section 11.3; its equilibrium nature was first described in Section 12.4 and there we wrote the equation for its partial dissociation.



Now, find  $\Delta G^\circ$  and find  $\Delta G$  for the following conditions.

$$[\text{CH}_3\text{CO}_2\text{H}] = 0.177 \text{ M} \quad [\text{H}^+] = 0.0016 \text{ M} \quad [\text{CH}_3\text{CO}_2^-] = 0.0521 \text{ M}$$

.....

This reaction involves ionic dissociation but recall that dissociation is only partial for weak electrolytes. Thus, we cannot equate CH<sub>3</sub>CO<sub>2</sub>H(*aq*) with H<sup>+</sup>(*aq*) + CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>(*aq*) as we had done for NaCl(*aq*) and anything else which is fully dissociated. In the case of weak electrolytes, the molecule itself and the dissociated ions are all present as their own chemical identities. Each item has its own thermodynamic values and you must keep them distinguished.

Start off by finding  $\Delta G^\circ$  from  $\Delta G_f^\circ$  values (one of which is zero and can be left out).

$$\begin{aligned}\Delta G^\circ &= \text{_____} (\text{_____ kJ}) - \text{_____} (\text{_____ kJ}) \\ &= \text{_____ kJ}\end{aligned}$$

The positive  $\Delta G^\circ$  reflects the weak acid aspect: if everything were to start at standard, then the forward reaction cannot happen by itself but the reverse can.

Now find  $\Delta G$  for the given conditions.

$$\Delta G = \Delta G^\circ + RT \ln Q = \text{_____ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln \frac{(\text{_____})(\text{_____})}{(\text{_____})}$$

$$\Delta G = \text{_____ kJ} + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(\text{_____...})$$

$$\Delta G = \text{_____ kJ} + (8.314 \text{ J/K})(298.15 \text{ K})(\text{_____...})$$

$$\Delta G = \text{_____ kJ} + \text{_____ kJ} = \text{_____ kJ}$$

Your answer is positive and the reaction is endergonic. At the given conditions, additional (net) dissociation cannot happen. The reverse process, which involves the recombination of the ions to form the neutral molecule, is spontaneous.

Enough for now.

#### 46.6 Keeping the perspective

In these three Chapters 44, 45 and 46, we have addressed the question of whether something can or cannot happen. We have seen that entropy answers that question but it is the total entropy,  $\Delta S_{\text{univ}}$ , which must be considered. We have seen how this breaks down into separate enthalpy and entropy parts for the system, as contained within the free energy relationship. We have seen how the quantitative aspects complement the qualitative discussions of prior Chapters. This had been forecast to you at the end of Chapter 40.

##### “ 40.5 Balance in perspective

In this and the last Chapter, we have applied principles for enthalpy and for entropy in our analysis of mixtures. In the five Chapters previous to the present two, we applied enthalpy and entropy to the simple phases. I have spent a lot of time on enthalpy and entropy because they are ultimately so important to so many things. It's not just about phases and about mixtures. It's about every process and every reaction. It's about everything that is possible and everything that will ever happen, biological or not. It's about your world, your universe.

I used enthalpy and entropy to explain phases but, all along, there has been another motive: I have used phases and mixtures to introduce you to the effects and the balance of enthalpy and entropy. From the existence of a simple phase to the construction of every membrane holding your cells together, enthalpy and entropy rule. Ironically, in the end, it is only entropy that rules on a grander scale, but enthalpy plays a role. We shall see this beginning in Chapter 44. It's important. It's very important.

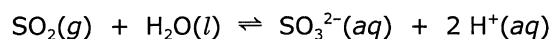
Remember the balance. You are being prepared for a relationship of universal proportions. But we're not there yet; that will come later. ”

We have completed most of this. Next, more of balance.

#### Problems

1. True or false.
  - a. Temperature can influence the sign of  $\Delta G$ .
  - b. Any reaction which is exergonic at standard conditions is exergonic at all conditions.
  - c. For any reaction, the allowed direction of net change is the endergonic direction.

- d. For any reaction at standard conditions,  $Q$  equals one.  
 e. Activities and reaction quotients are unitless.
2. What is the change in free energy (in kJ) at standard conditions for the combustion of 1.00 g  $\text{H}_2(g)$  to form  $\text{H}_2\text{O}(g)$ ?
3. a. Find  $\Delta H_{\text{vap}}^\circ$  (in kJ) and  $\Delta S_{\text{vap}}^\circ$  (in J/K) for methanol,  $\text{CH}_3\text{OH}(l)$ .  
 b. Use these to calculate the normal boiling point (in K) for  $\text{CH}_3\text{OH}(l)$ .
4. a. Find  $\Delta H_{\text{soln}}^\circ$  (in kJ) and  $\Delta S_{\text{soln}}^\circ$  (in J/K) for  $\text{CO}_2(g)$ .  
 b. Use these to calculate  $\Delta G_{\text{soln}}^\circ$  (in kJ) for  $\text{CO}_2(g)$  at 80. °C.
5. Write the  $Q$  expression for the following equations.
- a.  $\text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(l) \rightleftharpoons 2 \text{HNO}_3(aq)$   
 b.  $\text{MgCO}_3(s) + 2 \text{H}^+(aq) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$   
 c.  $\text{PbS}(s) + 2 \text{HF}(aq) \rightleftharpoons \text{PbF}_2(s) + \text{H}_2\text{S}(g)$
6. The following equation is balanced.



What is the value of  $Q$  for the following conditions?

$$0.0156 \text{ atm SO}_2 \quad 8.72 \text{ mol H}_2\text{O} \quad 0.0723 \text{ M SO}_3^{2-} \quad 0.0406 \text{ M H}^+$$

7. The following equation is balanced.
- $$2 \text{MnO}_2(s) + 4 \text{H}^+(aq) \rightleftharpoons 2 \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$$
- What is the value of  $Q$  for the following conditions?
- $$P(\text{O}_2) = 0.442 \text{ atm} \quad 11.3 \text{ mol H}_2\text{O} \quad 1.46 \text{ g MnO}_2$$
- $$[\text{H}^+] = 0.0438 \text{ M} \quad [\text{Mn}^{2+}] = 0.0673 \text{ M}$$

8. The following equation is balanced.
- $$2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$
- a. Find  $\Delta G$  (in kJ) for the following conditions at 298.15 K.  
 $P(\text{NO}_2) = 0.351 \text{ atm} \quad P(\text{N}_2\text{O}_4) = 4.52 \text{ atm}$
- b. From the given conditions, which direction is the exergonic direction: forward or reverse?

9. The following equation is balanced.
- $$\text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2 \text{HI}(g)$$
- a. Find  $\Delta G$  (in kJ) for the following conditions at 298.15 K.  
 $0.322 \text{ atm H}_2 \quad 0.440 \text{ mol I}_2 \quad 0.837 \text{ atm HI}$
- b. From the given conditions, which direction is the allowed direction of net change: forward or reverse?