

Chapter 44 CAN IT HAPPEN? Part 1

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Phases provide normal, everyday, observable experiences which allow us to apply the concepts of enthalpy and entropy, and to begin to understand the role of enthalpy and entropy in determining an outcome. But enthalpy and entropy assume pre-eminent roles in all things that happen, not just phases. We shall see their impact on all things as we go through this and many later Chapters. Along the way, we consider two fundamentally important questions related to anything you ever do, to any reaction ever run, or to any process whatsoever. Those two questions are the following.

1. Can the reaction or process happen?
2. If it can happen, then will it actually happen?

Can happen and will happen are different. Can happen relates to capability; will happen relates to actuality. We first distinguished these back in Chapter 18. It was a big part of our first entry into economics.

“ Economics

Energy is the economics of Nature. It makes things possible, although it doesn't necessarily make them happen. Energy is a capability to do something. It's like money. Money is the capability to buy and to do. (Sorry, Nature does not issue credit. You must have the energy at time of purchase.) Energy and money are capabilities. Having them means that things are possible, but it does not mean that those things will happen. You must understand this. If you have the money to buy the tablet, it does not mean that you will buy the tablet. You might save the money instead. Likewise, having energy means something can happen, but it does not necessarily mean that it will happen. If not used, the energy is saved (stored). Consider a can of gasoline which also has air inside it: this mixture of gasoline and air has the energy (capability) to blow up, but this doesn't happen by itself. There are actually two parts to this picture: whether something can happen and whether something will happen. These two parts will take some time to develop. We discuss only one aspect of can happen in this Chapter and into the next; we will postpone the rest until Chapter 44. The part of the picture dealing with will happen will start in Chapter 48. ”

In this Chapter and through Chapter 47, we discuss the aspects which determine whether a reaction can happen. Beginning in Chapter 48, we start into those aspects which determine whether a reaction which can happen actually will happen or not.

In order to go there, we need more entropy.

44.1 Entropy, qualitatively

To this point, the application of entropy has been related to phases and mixtures. We touched on this at various points in Chapter 34 by relating entropy to options.

“ At the most fundamental level, entropy involves the various options for energy. Entropy itself is a mathematical measure of the options for how the energy of a system is distributed among its various molecules and their various bonds and their various motions. Those energies are quantized, so this alone can impose some limits to the options. ”

“ For our discussion of phases, the options we need to consider for entropy are the options for location, orientation and motions of the particles involved. The options for location are related to the volume of the sample: a greater volume allows more options. Orientation relates to direction and whether the molecule is free to face in any direction. Motion can be how fast the particle moves in its phase and in what direction. Motion can also be more subtle things such as how the molecule vibrates along its chemical bonds or how the molecule rotates in three dimensions. All of these involve differing amounts of energies and that allows for more options. The more options, the better. ”

“ Entropy is important to all aspects of chemistry, not just phases. Entropy is a thermodynamic function and it shares many relationships which we have previously considered for enthalpy (H) and for internal energy (U) along with their changes, ΔH and ΔU ; these things go back to Chapter 18. Entropy is symbolized by S ; for any process or reaction, there is an associated ΔS , which is the final entropy minus the initial entropy, $S_{\text{final}} - S_{\text{initial}}$, for the system. The units for entropy are a bit different, however. Instead of just J's or kJ's as for ΔH or ΔU ,

entropy units also include a temperature component: the units are J/K. The connection with temperature has important ramifications because the total entropy contribution for a process can depend greatly on temperature. Our focus here involves the qualitative aspects of phases, and I don't want to get into the numbers and the units and the math of entropy yet. Later, beginning in Chapter 44, we will get into more details of entropy and we'll include quantitative (numerical) aspects and this business about increasing the entropy of the universe. I'm not interested in the universe right now. Right now, we're just doing phases. ”

Later is now. Now we will be doing the universe.

As previously described, entropy is connected to options. Ultimately, there is also a connection to probability and the likelihood of an outcome, based on the number of options which are available: simply stated, the outcome with the most options is the most likely outcome. There is a mathematical connection of entropy to options. In its barest form, the equation looks fairly straightforward.

$$S = k \ln W$$

S is entropy; \ln is natural logarithm; W is the number of options which are accessible given some amount of thermal energy in the system; k is called the Boltzmann constant. The Boltzmann constant is 1.381×10^{-23} J/K; it's the gas constant R (in its 8.314 J/K version) divided by Avogadro's number, which means it's on a per-particle scale and not a per-mol scale. (The above equation is actually engraved on Boltzmann's tombstone although it says log instead of \ln .) We will not do calculations with this equation because the numerical assessment of options is far beyond what we need (or want) to do here. Our qualitative connection between entropy and options will suffice for our purposes. Although you may be familiar with some aspects of options and of probability such as coin tosses or dice rolls, those are gross oversimplifications of chemical applications of probability. On the scale of one mole of particles, and given that each particle has a large number of options available at normal temperatures, the grand totals for options in a chemical system get into incomprehensibly large numbers such as $10^{1,000,000,000,000,000,000,000,000}$; that's ten raised to the power of a trillion trillion, and that is one enormous number.

As introduced in Chapter 34, the options of which we speak are the options for how the energy within a given system of some particles is distributed at some set of conditions. As quoted above from that Chapter, the energy is distributed among the various options for location, orientation and motions. At this time, we will get a bit picky with the terminology and break these aspects into specific and more traditional classifications.

"Translational energy" is the energy of moving through space at some velocity. (The word "translation" is commonly associated with languages but another dictionary definition does relate it to movement.)

"Rotational energy" is the energy of spinning (rotating) at some speed. This may sound simple but the spinning can be broken into three dimensions and this can get complicated depending on the shape of the molecule.

"Vibrational energy" is the energy associated with the springiness of bonds and of bond angles. As noted in Section 25.4, bonds stretch and contract, back and forth, quite a bit although there is a representative length which we call the bond length. We can also now add that bond angles can bend and flex more open and more closed a bit, also around some representative value. All of these motions are considered vibrations.

We could even go back as early as Chapter 20 with the energies of electrons in the orbitals in atoms and, later, in polyatomics. In the current context, that contribution is called "electronic energy". All of translational, rotational, vibrational and electronic energies are quantized. At typical temperatures, most substances are in their electronic ground state so that is the only option for electronic energy. (Delocalized networks, Section 33.3, are exceptions.) Also near typical temperatures, vibrational motions are commonly in ground states although higher states do become accessible at higher temperatures. On the other hand, the energy spacings are small for rotational levels and very small for translational levels, and this allows molecules to take on one of a wide range of rotational energies and one of a wide range of translational energies. Ultimately, this allows for many options for chemical units with respect to how fast they can rotate or move through space. These options are greatest for individual molecules flying around in a gas phase. In a solid phase, the particles are packed in and caged by their neighbors. This imposes restrictions on many of the usual motions although wiggling in place remains possible. Liquids are of intermediate options. In all considerations, the important consequence of more and more options is that it allows the energy to be distributed in more and more ways. That is Nature's intention and that will become the law.

Notice again the mention of temperature. This is for a very good reason: entropy is linked to temperature. For any substance in any phase, higher temperatures always allow for more options for motion. For example, higher temperatures allow for faster speeds and faster rotations. Since more options become available, entropy always increases as temperature increases. Here's another way of looking at it. If there was no thermal energy, then multiple options could not exist. In fact, if you could make a perfect crystal at 0 K, then all molecules in that crystal would be in their electronic, vibrational, rotational and translational ground states. Without any thermal energy whatsoever, that would be the only option available. Arithmetically, under these conditions, the number of options (W) equals one; plugging that into the above equation gives us

$$S = k \ln(1) = 0$$

which means there is no entropy in that crystal. But that's at 0 K. Once the sample starts to acquire any heat whatsoever, rotational and translational options become available and the entropy increases rapidly and in huge amounts. By normal temperatures, the numbers of options are beyond astronomical.

Thus, within the equation $S = k \ln W$, there lies a connection for energy, temperature and the number of options. We can summarize this by saying that entropy is a measure of the options for the motional energy of a system at some specified temperature.

The details of entropy get more complicated than what I've presented here and we need not go further for our purposes. Suffice it to say that options are extremely important for how energy can be distributed within one molecule and then within the huge numbers of molecules in a given sample at some temperature. This can then affect physical and chemical outcomes on a bigger scale. In previous Chapters, we have seen that options affect which phases are adopted at what conditions; we have seen that options affect whether two compounds can mix; heading in our current direction, we will see that options will affect whether a chemical reaction can occur. The outcome of every process is in the direction which increases the options for how energy is distributed. This is very important but the ramifications may not be obvious. Let me give an illustration.

Consider some system which contains one or more substances at some set of conditions and which includes some total energy. What can happen with this system? Can it react to form one set of products? Can it react to form another set of products? Can it undergo some phase change? Or can it just remain there, unchanged? Which outcome is most likely? Given two or more possible outcomes for some set of conditions, the outcome with the most options is the most favored to occur (although this does not mean that it will occur).

There is a catch to all of this. Although our emphasis so far has been on the system, we must look beyond the system and include the surroundings. While Nature always seeks to increase the distribution of energy among as many options as possible, this applies to the grand total of system and surroundings. Whenever an exothermic or endothermic process occurs, there is a transfer of heat between the system and surroundings. For an exothermic process, J's leave the system and go to the surroundings, thereby increasing options (entropy) in the surroundings. For an endothermic process, J's are gained by the system from the surroundings, thereby decreasing options (entropy) in the surroundings. Ultimately, our total entropy picture must take into account both the system and surroundings. Sound complicated? This pursuit could easily fall into a chasm of spontaneous mayhem but, fortunately, this breaks down into a very simple relationship. We shall see this in the next Chapter.

Instead of analyzing the many options quantitatively, which would be extremely tedious, we work with the logarithmic function called entropy. Entropy is our guide. Entropy is our tool. Entropy is also the law. We will spell out the law in the next Chapter. At this time, we need to introduce some quantitative aspects of entropy.

44.2 Entropy, quantitatively

As first noted in Chapter 34 and as quoted upstairs, entropy is a thermodynamic function depending on the specific state of the system. As such, several aspects parallel those for enthalpy and internal energy, although there are some differences. The delta functions are the same for all. For all, only the final and initial states count; the middle does not matter.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} \qquad \Delta U = U_{\text{final}} - U_{\text{initial}} \qquad \Delta S = S_{\text{final}} - S_{\text{initial}}$$

For each of these, we can specify standard conditions, which again refers to a process which begins at standard conditions and ends at standard conditions.

$$\Delta H^\circ = H_{\text{final}}^\circ - H_{\text{initial}}^\circ \qquad \Delta U^\circ = U_{\text{final}}^\circ - U_{\text{initial}}^\circ \qquad \Delta S^\circ = S_{\text{final}}^\circ - S_{\text{initial}}^\circ$$

There are two key differences between entropy and enthalpy or internal energy. One has already been mentioned: H° and U° take straight energy units of J's and kJ's, while entropy takes units of J/K which reflects its connection to temperature. (OK, technically, we can incorporate a "per mol" term into these. This was mentioned for ΔH° back in Chapter 19, where some values could be taken as kJ or as kJ/mol. Likewise, S° can be taken as J/K or as J/(K·mol). As was done in Chapter 19, we will be a bit loose with using the per mol term.) The other key point is that actual values for S° of substances are measurable; these are called standard entropies (or standard molar entropies). Recall from Chapter 18 that specific values for H° or for U° are not known. Instead, as developed in Chapter 19, calculations of ΔH° utilized enthalpies of formation, ΔH_f° ; these enthalpies of formation are relative to setting $\Delta H_f^\circ = 0$ kJ for standard element reference forms. We won't need that approach for entropies; we'll just be using S° directly. Even the standard element reference forms have measurable entropies, so those will not be zero.

Values of standard entropies, S° , are determined as a function of temperature and the energy which is required to heat a mole of sample from 0 K to that temperature. This process includes heat capacity, which is associated with warming, and it also includes any phase change which might be encountered on the way. Ultimately, the grand total of all those J's is distributed among all the options available to that compound in that phase at that specified temperature. Let me bring back a sentence from Section 18.5 when we first talked about heat capacity.

“ Every different compound has a different specific heat capacity because every different compound responds to heat energy differently. ”

There's an important connection to make at this time: every different compound responds to heat energy differently because every different compound has its own set of options for how it distributes that energy among its many motions.

All pure substances by themselves have positive values for S° . This much also differs from values of ΔH_f° since those can be positive or negative for different substances and they are zero for reference elements. Although values of S° are always positive for pure substances, values of S° for a solute can be positive or negative. That's because the values take into account the entropy of the solvation interaction from surrounding solvent molecules. This is somewhat of a minor technical point; it won't change the general calculations.

As in the case of ΔH_f° , values of S° for many substances have been tabled over the years and some are included in Appendix A. Now, let's start looking at some numbers for entropies.

We introduced entropy within the context of phases so we'll work with some of those values first. Let's bring back the phase relationships from Chapter 34.

phase:	(s)	(l)	(g)
entropy, S :	little	moderate	a lot
IFs:	stronger	somewhat strong	very little (if any)
	—— gap ——		———— big gap ———

We're focusing on entropy right now and not IFs, so we'll take IFs out of the chart. Let's look at some values of S° for one mol of water at 0 °C.

phase:	(s)	(l)	(g)
S° (0. °C):	41.33 J/K	63.33 J/K	185.90 J/K
	—— gap ——		———— big gap ———

I chose standard entropies at 0 °C, instead of the usual 25 °C, in order to include a realistic temperature for all three phases. Notice how the differences in the values for S° reflect the gap/big gap relationship. We can also consider the values for 25 °C for (l) and (g).

phase:	(s)	(l)	(g)
S° (0. °C):	41.33 J/K	63.33 J/K	185.90 J/K
S° (25 °C):		69.95 J/K	188.83 J/K
	—— gap ——		———— big gap ———

Notice that the entropies are indeed higher at the higher temperature.

These values allow for calculations of ΔS° for phase changes. For example, consider the vaporization of one mol of water at 25 °C.

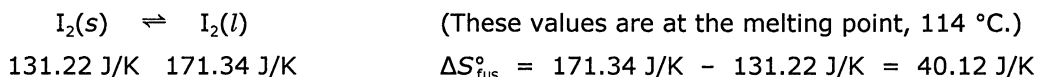
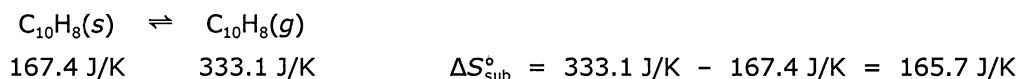
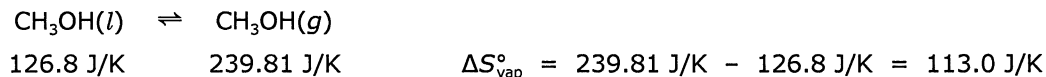


We can calculate $\Delta S^\circ_{\text{vap}} = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$.

$$\Delta S^\circ_{\text{vap}} = 188.83 \text{ J/K} - 69.95 \text{ J/K} = 118.88 \text{ J/K}$$

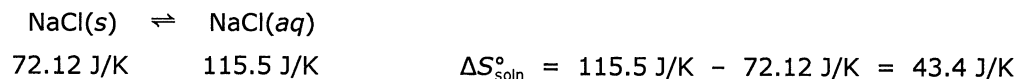
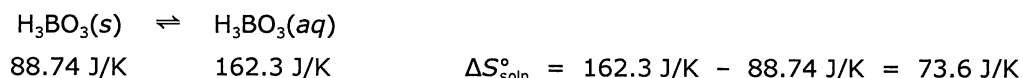
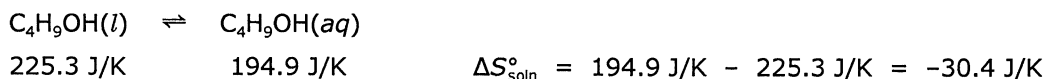
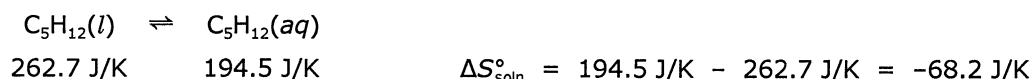
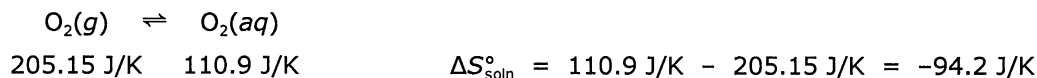
Thus, the system gains 118.88 J/K for the vaporization of one mol of water. This is a sizeable entropy increase for a simple process. That clearly reflects the greater entropy associated with the gas phase.

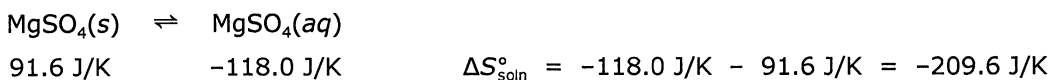
Here are some more examples of entropies of phase change for one mol of other substances.



All of these examples have positive ΔS° for the direction as written and all are therefore favored by entropy. Notice that production of a mole of gas gives a large increase in entropy. This is a simple consequence of the fact that there are just so many more options for gas phase than for the other common phases.

Now fast forward to Chapter 40 and return to the entropy of solution. We'll consider some of the those substances dissolving into water.



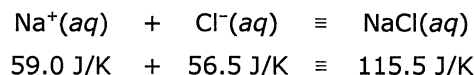


Take a look at the numbers. Some of those dissolutions are favored by entropy (positive $\Delta S_{\text{soln}}^{\circ}$) and some are disfavored by entropy (negative $\Delta S_{\text{soln}}^{\circ}$). The dissolving of gases into water is always disfavored by entropy, and substantially so. Liquids which are primarily hydrocarbon deadspace are also disfavored by entropy for dissolving in water, but liquids which have considerable hydrogen bonding can be favored. Molecular solids will tend to be favored by entropy (although some can be disfavored). Ionic solutes can go either way. Go back to Chapter 40 and read the sections related to the examples which are now shown here with numbers.

Let me add two points about ionic solutes.

First, it is possible to assign entropies to individual ions in solution if we just want to focus on one ion at a time. There is a problem with this, however: although you can measure the entropy of a compound in water, you cannot directly measure the entropy of one ion by itself in water. The reason is simple: you can't just dump one mole of one ion into water. Instead, you will always have some cation/anion combination in any real compound. To get around this limitation, a reference ion is selected and assigned a zero value; all other ions are measured relative to that. The selected reference ion is again $\text{H}^+(aq)$, as first noted in Chapter 19 for ΔH_f° purposes. Now, $S^{\circ} = 0$ (defined as exact) for $\text{H}^+(aq)$. Relative to this, the standard entropies for many individual ions have been determined and some are listed in Appendix A. Some ion values are positive and some are negative, but that just means they are greater than or less than $S^{\circ} = 0$ for $\text{H}^+(aq)$.

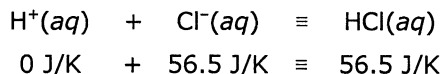
The second point to note for ionic compounds in solution is that we are still assuming full dissociation. This allows us to represent an ionic solute either as the neutral compound or as the separate ions. For example, writing $\text{NaCl}(aq)$ is equivalent to writing $\text{Na}^+(aq) + \text{Cl}^-(aq)$. You won't find $\text{NaCl}(aq)$ in Appendix A, although you will find $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$; the value of S° for $\text{NaCl}(aq)$ is the sum of the S° values for $\text{Na}^+(aq) + \text{Cl}^-(aq)$.



This notion was first introduced in Section 19.3 and repeated in Section 39.4 regarding enthalpies. The connection to net ionic format for balanced equations was also made beginning in Section 19.3.

“ Here's an important point to note: if any reagent in an aqueous reaction is a strong electrolyte, then you must work in net ionic format for the balanced equation. Tables of ΔH_f° values are generally compiled for the net ionic approach. If you check Appendix A, you will find $\text{NaCl}(s)$ but you will not find $\text{NaCl}(aq)$. In net ionic format, $\text{NaCl}(aq)$ would be written as $\text{Na}^+(aq) + \text{Cl}^-(aq)$; ΔH_f° values for both of those ions are in Appendix A and you add them together to get the value for $\text{NaCl}(aq)$. This is important now and it will be important later in Chapters 39 and 44. ”

Later is now. The same considerations apply to standard entropies. And, by the way, back then we were dealing with ionic compounds, but this also applies to any strong electrolyte. For example, the standard entropy for hydrochloric acid can be derived as follows.

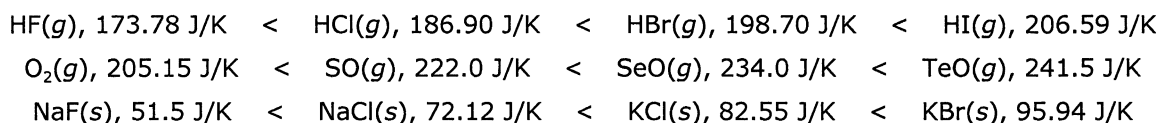


(The zero for $\text{H}^+(aq)$ is exact, so it does not affect round-off.) Note: these relationships apply to strong electrolytes but not to weak electrolytes. For example, thermodynamic values for $\text{CH}_3\text{CO}_2\text{H}(aq)$ are NOT equivalent to the sum of values for $\text{CH}_2\text{CO}_2^-(aq)$ and $\text{H}^+(aq)$. (You can check those values in Appendix A.) For weaks, since they are not fully dissociated, each chemical unit has a separate value.

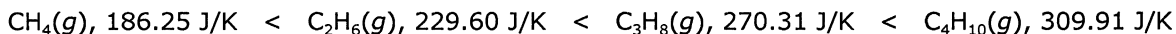
This ends the two points for ionic solutes.

So far, our quantitative aspects have emphasized ΔS° for changes in phases. What about the actual values of S° for compounds by themselves? Take a look at the various numbers above: values of S° for actual substances commonly range from tens through several hundreds of J/K. There are two very general trends to mention: standard entropies typically increase with the mass of the chemical unit and with the number of atoms bonded within the chemical unit. Of course, increasing the number of atoms in a chemical unit also increases its mass, so these effects can overlap. The mass effect is readily seen

when comparing similar compounds which contain different atoms from within a Group in the Periodic Table. For example, compare the following values of S° .



For the trend related to the number of atoms, one can compare compounds of the same elements but different numbers of atoms. This will also include a mass effect, but the result is greater than a mass effect by itself. In the following series, the number of atoms and the mass increase, as does S° .



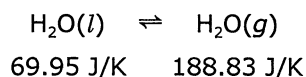
Comparisons between similar compounds as in these examples are useful but the trends may not be as reliable when comparing very different types of compounds. That's because there are subtle complications which can also arise. One important point which must be emphasized is that all such comparisons must be made for compounds of the same phase. Different phases can have a large effect on entropy, and that effect is separate from the effects of mass and number of atoms. For example, S° for $\text{C}_5\text{H}_{12}(l)$ is 262.72 J/K, and that is out of trend with S° for the hydrocarbons above. That value of 262.72 J/K is for liquid phase, however, and the values above are for gas phase. If we compare the value for $\text{C}_5\text{H}_{12}(g)$, then S° is 349.56 J/K, which is fully in line with the above values.

OK, we've looked at some numbers and some trends for S° . Now we need to address arithmetic relationships dealing with these.

44.3 Entropy, arithmetically

We actually touched on some preliminary aspects of the math above when we derived ΔS° of phase changes. We will now expand this to any type of process or reaction. Before going there, let's return to all four Important Aspects from Chapter 19. These now also apply to entropy.

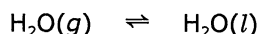
We've already touched on Important Aspect 1 by noting that $\Delta S^\circ = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$. For Important Aspect 2, consider again the vaporization of water at 25 °C



for which $\Delta S^\circ_{\text{vap}} = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$.

$$\Delta S^\circ_{\text{vap}} = 188.83 \text{ J/K} - 69.95 \text{ J/K} = 118.88 \text{ J/K}$$

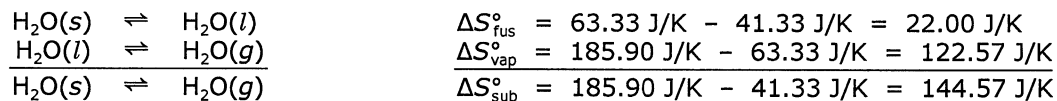
Now consider the reverse process, condensation,



and you can see that $\Delta S^\circ_{\text{con}} = -\Delta S^\circ_{\text{vap}} = -118.88 \text{ J/K}$. Thus, Important Aspect 2 applies.

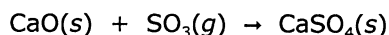
For Important Aspect 3, the amounts are for the equations as written; thus, vaporization of one mole of $\text{H}_2\text{O}(l)$ gives an increase in entropy of 118.88 J/K, while vaporization of two moles gives an increase of 237.76 J/K.

For Important Aspect 4, we can again invoke the additivity of reactions. For example, working with the previous 0. °C values for water, we have the following additivity.

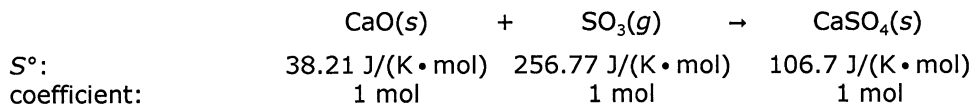


Thus, all of these Important Aspects still apply. If you need to refresh the four Important Aspects from Chapter 19, then do it.

We now consider how to determine ΔS° for any reaction whatsoever. This follows the same procedure as for ΔH° in Chapter 19, namely products minus reactants, each multiplied by its coefficient from the balanced equation. Whereas ΔH° was derived from values of ΔH°_f , ΔS° will derive from S° . We'll start simple: find ΔS° for the following equation.



You'll need some values from Appendix A.



Set up products minus reactants. As usual, all mol terms drop out.

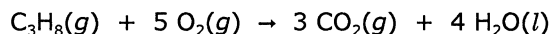
$$\Delta S^\circ = 1(106.7 \text{ J/K}) - 1(38.21 \text{ J/K}) - 1(256.77 \text{ J/K}) = -188.3 \text{ J/K}$$

Note that there is a sizeable drop in entropy with this reaction. Most of that is due to the loss of one mole of a gas phase component in the equation. As was seen earlier for phase changes, the loss or gain of gas phase components will have a big effect on ΔS° for any reaction or process.

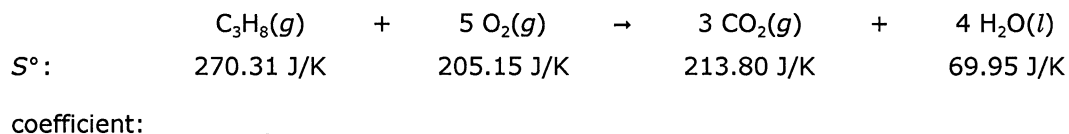
As we had done for ΔH° in Chapter 19, we will follow the sigfig rule which was given at that time for simplicity. In other words, for calculating ΔS° from products minus reactants, use the +/- rule and round off according to the value of S° with the fewest decimals. In this example, the answer was rounded to one decimal due to the one decimal in the value for S° of $\text{CaSO}_4\text{(s)}$.

That was a very simple example with all coefficients of one. Let's complicate things a bit. We'll bring back the combustion of propane from Example 4 in Chapter 19. We did the calculation for enthalpy of combustion back then; now do it for the entropy of combustion.

Example 1. Find ΔS_c° for propane, using the same equation as in Chapter 19.



You'll need a few values for S° . You can leave out the mol units.

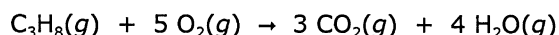


Plug everything in.

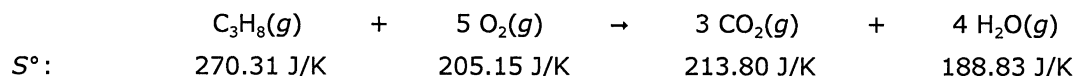
$$\Delta S_c^\circ = \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) + \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) - \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) - \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K})$$

Punch it out and round it off: you get $\Delta S_c^\circ = -374.86 \text{ J/K}$. That's a big drop in entropy but notice what happens during the reaction: the system starts with six moles of gases and ends up with only three moles of gases. The loss of three moles of gas phase molecules accounts for the majority of the entropy loss. For a comparison, you can repeat the same calculation but now with the H_2O product in the gas phase.

Example 2. Find ΔS_c° for propane, now involving $\text{H}_2\text{O(g)}$ as a product.



Put it all together.



$$\begin{aligned} \Delta S_c^\circ &= \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) + \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) - \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) - \underline{\hspace{1cm}} (\underline{\hspace{1cm}} \text{ J/K}) \\ &= \underline{\hspace{1cm}} \text{ J/K} \end{aligned}$$

How does that compare? The system still starts with six moles of gas but now it ends with seven; as a result, ΔS_c° is positive. If you want to check your answer, this reaction is used again in the next Chapter; it's right before Example 1.

This bit about ΔS° and gas phase molecules is an important point. We see it here in these reactions and we saw it in the phase change calculations earlier. The impact of the gas phase on the entropy of a reaction or process can be summarized as follows.

Increasing the number of moles of gas phase molecules in a system favors entropy and increases ΔS° . (ΔS° will be more positive or less negative.)

Decreasing the number of moles of gas phase molecules in a system disfavors entropy and decreases ΔS° . (ΔS° will be less positive or more negative.)

These effects are substantial and they are often greater than the entropy changes due to the changing compounds themselves. On the other hand, solid and liquid phases have only a modest impact. Solution phases can have a modest impact or a large impact, positive or negative, and this depends on the solute. This can be seen in a few of the cases illustrated earlier.

This is enough for now with number crunching. As noted, there is a lot of parallel to the number crunching of Chapter 19. There are other considerations, too, which we will encounter.

Problems

- True or false.
 - The standard entropy of every ion is a negative number.
 - The evaporation of any liquid has a negative ΔS° .
 - The formation equation for $\text{H}_2\text{O}(l)$ has a positive ΔS° .
 - The sign of ΔS° for every sublimation is positive.
 - The standard entropy for $\text{H}^+(aq)$ is zero.
 - All neutral substances have $S^\circ > 0$.
 - S° for standard reference elemental forms is zero.
- In each of lines a and b below, which entry has the largest S° ?
 - $\text{O}_2(g)$ $\text{F}_2(g)$ $\text{Br}_2(g)$ $\text{Br}_2(l)$
 - $\text{CH}_3\text{OH}(g)$ $\text{CH}_3\text{OH}(l)$ $\text{CH}_3\text{OH}(aq)$ $\text{CH}_4(g)$
- In each of lines a and b below, which entry has the largest S° ?
 - $\text{N}_2(g)$ $\text{NF}_3(g)$ $\text{PF}_3(g)$ $\text{PF}_5(g)$
 - $\text{AsH}_3(g)$ $\text{H}_2\text{S}(g)$ $\text{H}_2\text{O}(g)$ $\text{NH}_3(g)$
- Calculate ΔS° (in J/K) for the following balanced equation.

$$3 \text{N}_2\text{O}(g) + 2 \text{NH}_3(g) \rightarrow 4 \text{N}_2(g) + 3 \text{H}_2\text{O}(g)$$
- Calculate ΔS° (in J/K) for the following balanced equation.

$$2 \text{FeO}(s) + \text{Cl}_2(g) + 4 \text{H}^+(aq) \rightarrow 2 \text{Fe}^{3+}(aq) + 2 \text{Cl}^-(aq) + 2 \text{H}_2\text{O}(l)$$
- Calculate ΔS° (in J/K) for the neutralization reaction of aqueous nitric acid with aqueous potassium hydroxide.
- Consider each of the following balanced equations.
 - $\text{MgO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Mg}(\text{OH})_2(s)$
 - $2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g)$
 - $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{HCl}(g)$
 - $\text{Na}_2\text{CO}_3(s) \rightarrow \text{Na}_2\text{O}(s) + \text{CO}_2(g)$
 - $2 \text{C}_2\text{H}_2(g) + 5 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$
 - Which one will have the most positive ΔS° ?
 - Which one will have the most negative ΔS° ?