

Chapter 45

CAN IT HAPPEN? Part 2

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We continue in the journey which addresses the question of whether a reaction can or cannot happen. Along this path, we will encounter the law. But first, we have to deal with a tricky term.

45.1 Spontaneous

I now introduce one of the trickier words in all of chemistry: spontaneous. This word has been used for many years in thermodynamic applications, but this one word causes a lot of confusion to a lot of people. The reason for the confusion is that the word has a normal, everyday definition but it has a very specific chemistry definition which is related to, but critically different from(!), the normal everyday definition. The confusion arises from not understanding the critical distinction.

As used in normal everyday language, spontaneous basically means "happens by itself". Thus, in such a context, a process is spontaneous when it actually happens on its own. This is NOT the chemistry meaning of the word. In chemistry, spontaneous gets a subtly different definition: spontaneous means "can happen by itself under the given conditions". Notice that the definition only deals with can happen; it does not say that it actually will happen. A process can be spontaneous but it may never actually happen. You must understand this distinction.

The property is called spontaneity. Spontaneity refers to the capability to occur and not to whether it does occur. If a reaction or process cannot occur by itself under the given conditions, then we say that it is nonspontaneous or simply not spontaneous.

Another term which can also be used here is allowed. A spontaneous process is an allowed process; it can happen by itself under the given conditions. The opposite of allowed is forbidden. A nonspontaneous process is forbidden; it cannot happen by itself under the given conditions. Let's summarize these terms for emphasis and distinction.

If a process can happen by itself under the given conditions, then we can say the process is allowed or we can say the process is spontaneous.

If a process cannot happen by itself under the given conditions, then we can say the process is forbidden or we can say the process is not spontaneous.

Remember! None of this even addresses the question of whether it will actually happen or not. That is a separate issue. There is more to whether something will happen and we will see that part beginning in Chapter 48.

You may have noticed that the phrases "by itself" and "under the given conditions" are attached to can or cannot happen. Those phrases are very important. "By itself" means the system can undergo the process by itself and the energy is right to do so. The "given conditions" are important because, if you change the conditions, then you can change between a spontaneous and a nonspontaneous outcome. If a process is nonspontaneous (cannot happen by itself under the given conditions) but you still want it to happen, then you must pay energy into the system.

Actually, it's not really the energy of the system which is of absolute importance to spontaneity. It's the entropy of the universe which we need to consider.

45.2 A universe of options

It is time to take on the universe.

Well, no, we won't be taking on the whole universe. The use of the word universe is an exaggeration but it's part of the historical terminology of thermodynamics. Here's how we first introduced this in Chapter 18.

“ There are two terms which have a somewhat specific meaning but which are derived from normal words: "system" and "surroundings". The system is the sample under study. It will undergo some change. It's whatever we define it to be for the study at hand. It can be some neutralization reaction in a beaker. It can be the combustion of hydrogen in air. It can even be something as simple as an ice cube melting. The surroundings are the environment of the sample. On a practical basis, the surroundings can be taken as the immediate environment with which the sample interacts or, technically, the surroundings can be the rest of the universe. ”

Thus, the historical breakdown is to distinguish one's system from its surroundings; these then make up the grand total, designated the universe.

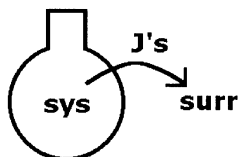
$$\text{universe} = \text{system} + \text{surroundings}$$

Some sources simply refer to total. In actuality, most studies are limited to the immediate surroundings anyway. Thus, we can also present this as the following.

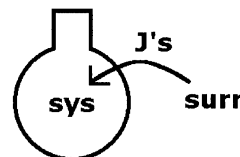
$$\text{total} = \text{system} + \text{surroundings}$$

For our purposes here, both of these statements will be equivalent. I'll usually use universe but your instructor may just use total. "Universe" may seem a tad extreme, but if you ever get into the energies of an exploding supernova at 1.2 gajillion light years away, then universe does become an appropriate term.

Let's bring back our illustrations from Chapter 18.



exothermic (J's exit system)
system gives J's to surroundings
enthalpy of the system decreases
 $H_{\text{final}} < H_{\text{initial}}$
 ΔH is negative



endothermic (J's into system)
system gets J's from surroundings
enthalpy of the system increases
 $H_{\text{final}} > H_{\text{initial}}$
 ΔH is positive

Back then, the conservation rules were stressed.

“ Throughout all of these discussions, keep in mind the conservation of energy. The total J's between the system and the surroundings stay the same. J's don't just appear and disappear. If the system loses 5 J, then those 5 J are out there in the surroundings. Energy is conserved. And, like always, mass is conserved. Grams are conserved. Joules are conserved. Together, it's the conservation of mass/energy, or the conservation of g's and J's. ”

Summarily,

$$\Delta H_{\text{sys}} = -\Delta H_{\text{surr}}$$

and that always applies. Whatever one gains, the other loses.

Now we introduce a key distinction between ΔH and ΔS . The J's of enthalpy are always conserved, but the J/K units of entropy will not be conserved while any reaction or process is occurring. In fact, the total entropy will be increasing. We will see this as we develop this picture.

Before we proceed, let me note that there are variations to this picture which depend on the conditions of the system and the surroundings. We are going to keep our coverage at the basics. I will present one of the most common derivations although there are others. For example, we will develop the picture with enthalpy; another derivation uses internal energy. Be aware that such variations and other conditions exist.

OK, you are now ready to face the law. We will now tackle the question of whether any specific reaction or process can or cannot happen.

45.3 The law

We have alluded to this previously.

Section 34.2:

“ ... Nature demands higher entropy; all processes must increase entropy, and only those events which increase the total entropy in the universe can occur. ”

Section 44.1:

“ 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. ”

Thus, the law, and the simple question of whether a reaction or process can or cannot happen, comes down to a very simple matter: the reaction or process must result in more options overall.

THE ENERGY OF THE UNIVERSE IS CONSTANT AND CONSERVED, BUT THE NATURAL DIRECTION IS TO INCREASE THE SPREAD OF THAT ENERGY ACROSS AS MANY WAYS AS POSSIBLE.

That direction is the law and it is reflected in an increase in entropy, specifically an increase in the grand total, S_{univ} . In other words, any reaction can happen by itself under the given conditions if it results in an increase in total entropy. We can also say that ΔS_{univ} must be positive. If the reaction would instead result in a decrease in S_{univ} , which amounts to a negative ΔS_{univ} , then it cannot happen by itself under the given conditions.

But wait, you say, what about enthalpy? After all, we had talked about phases as a result of the balance of entropy and enthalpy. We had talked about solutions which may be favored or disfavored by enthalpy or entropy or both. What happened to enthalpy in this law?

Enthalpy is part of this picture by its connection to the heat which is transferred between the system and the surroundings, as quoted above in the paragraph from Chapter 44. The transfer of heat causes a change in entropy given by

$$\Delta S = \frac{\Delta H}{T}$$

and whoever (system or surroundings) is gaining the heat (enthalpy) is then also gaining entropy; whoever is losing the heat is losing entropy. This part of the change in total entropy is in addition to the change in entropy within the system which occurs as a result of the reaction or process itself. In other words, the total change in entropy, ΔS_{univ} , derives from two sources.

Within the system as a reaction occurs, chemical identities change and/or phases change. Since the components of the system change, then the entropy of the system changes. This change is designated ΔS_{sys} .

As a result of the reaction in the system, heat may be exchanged with the surroundings. The gain or loss of heat by the surroundings gives a change in entropy of the surroundings which is designated ΔS_{surr} .

We can summarize these two contributions to ΔS_{univ} by

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Ultimately, "can happen" requires an increase in S_{univ} which is the same as saying ΔS_{univ} must be positive. This is the basic requirement for the law. We can connect ΔS_{univ} to ΔS_{sys} and ΔS_{surr} by this equation but we would like to focus our attention only on our system of interest, without worrying about the surroundings. Through a suitable derivation, we can convert all parameters to those of the system and this makes everything more convenient.

To do this derivation, we start with the change in entropy of the surroundings due to the heat transferred.

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T}$$

Energy conservation requires that

$$\Delta H_{\text{surr}} = -\Delta H_{\text{sys}}$$

so we can combine these last two to get

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

and this gives us a connection between the surrounding's ΔS_{surr} and the system's ΔH_{sys} . (By the way, in the derivation we use here, T will be the same for system and surroundings so we need not distinguish T_{sys} versus T_{surr} .) This equation tells us the impact on the entropy of the surroundings as a result of the endothermic or exothermic reaction in the system. If the system releases heat to the surroundings (exothermic process), then the surroundings gain heat and therefore the entropy of the surroundings increases. If the system absorbs heat (endothermic process), then the surroundings lose that heat and lose entropy as a result.

Now, put this back into ΔS_{univ} .

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}\end{aligned}$$

Voila! We now have an equation which relates the critical parameter ΔS_{univ} to system terms only. We no longer need to keep track of the surroundings at all. Keep in mind, however, that the surroundings' entropy contribution to the total is embodied within $\Delta H_{\text{sys}}/T$ and that this is the result of the transfer of heat. On the other hand, the ΔS_{sys} term is not due to heat transfer; it is the change in entropy due to the change in the molecules or phases of the system components.

While this equation provides the answer to whether a reaction or process is allowed or not, it is common and useful to take this derivation a bit further and work with energy units and not entropy units. To do this, multiply everybody by temperature.

$$T \Delta S_{\text{univ}} = T \Delta S_{\text{sys}} - \Delta H_{\text{sys}}$$

The $T \Delta S$ term is an energy term, in units of J's or kJ's. This equation is now the amount of energy ($T \Delta S_{\text{univ}}$) which is possible or which can become available during the course of an allowed reaction. The actual kJ's can come from the system and/or they can come from the surroundings but the value $T \Delta S_{\text{univ}}$ must be greater than zero for spontaneity. Since this represents energy to be released, and since energy released is taken as negative, we negate the above equation

$$-T \Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

and we then take this one more step to its final working form. We define a new function, given by $\Delta G_{\text{sys}} = -T \Delta S_{\text{univ}}$.

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

G is called the Gibbs energy. The delta function, ΔG , is the change in Gibbs energy for a reaction or process. Notice that ΔG is given in terms of the system, ΔG_{sys} , although it is set equal to the universe term, $-T \Delta S_{\text{univ}}$. That's because all of this is the result of some reaction or process occurring within the system of study. That reaction or process within the system ultimately gives rise to the total effect given by $-T \Delta S_{\text{univ}} = \Delta G_{\text{sys}}$.

We can add ΔG to our list of thermodynamic delta functions.

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

Traditionally, the delta function, ΔG , has been called the free energy and we will primarily use that term. The "free" in free energy has nothing to do with the notion of no-cost. Instead, "free" means available, much like a person who is "free" to do other things. ΔG is the amount of energy associated with some process which is available after fulfilling the requirement to increase total entropy; or, more simply, ΔG is the theoretical maximum amount of energy which becomes available from an allowed process. Available means that it can be used to accomplish some task in the surroundings.

There's a catch with the part about "theoretical maximum". Under some conditions, we can get close to the theoretical maximum but, usually, we get less than the max. There are numerous reasons for that but we won't go into them. Just understand that the kJ's of a ΔG_{sys} represent a theoretical maximum which could be made available under perfect circumstances.

The equation above with $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$ is our working equation for fulfilling the law regarding whether a reaction can happen or not. In Chapter 19, we learned how to calculate enthalpies of reaction from enthalpies of formation. In Chapter 44, we learned how to calculate entropies of reaction from molar entropies. Together and with T , these will give ΔG for that reaction and we'll see those calculations later. For now, it is the sign of ΔG that is important because that determines spontaneity. Remember that ΔG was set to a negative function of ΔS_{univ} , so these two will always have opposite signs. We can summarize the following three cases. I will include two new terms: "exergonic" and "endergonic". They apply to the sign of ΔG_{sys} . Note! They parallel the use of "exothermic" and "endothermic" for ΔH_{sys} but don't confuse them.

- CASE 1 ΔS_{univ} is POSITIVE which means ΔG_{sys} is NEGATIVE.
 S_{univ} increases during the process.
 G_{sys} decreases during the process.
 The process can happen by itself under the given conditions.
 The process is allowed.
 The process is spontaneous.
 The process is exergonic.

For these, the number of kJ's given by ΔG_{sys} is the theoretical maximum which are available from the process.

- CASE 2 ΔS_{univ} is NEGATIVE which means ΔG_{sys} is POSITIVE.
 S_{univ} decreases during the process.
 G_{sys} increases during the process.
 The process cannot happen by itself under the given conditions.
 The process is forbidden.
 The process is not spontaneous.
 The process is endergonic.

For these, the process cannot happen by itself BUT there's a kicker: it can happen if we pay into it! This gives a new meaning to the number of kJ's given by a positive ΔG_{sys} : this number is the theoretical minimum which we must pay into the process in order for it to happen. This is a theoretical minimum payment. Under certain conditions, we will get by with close to this amount but, usually, we need more than that.

By the way, free energy also follows the four Important Aspects as for enthalpy (Chapter 19) and for entropy (Chapter 44). Right now, let me deal with Important Aspect 2, which relates to reversing an equation and negating the sign of the delta function. For this Case 2, the positive ΔG_{sys} means the process cannot happen by itself. On the other hand, the reverse process will have negative ΔG_{sys} and is therefore allowed. Thus, a nonspontaneous process as written will always be spontaneous in the reverse direction.

Now, our final Case.

- CASE 3 ΔS_{univ} is ZERO which means ΔG_{sys} is ZERO.
 S_{univ} stays the same.
 G_{sys} stays the same.

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

All three of these Cases are extremely important. Get them down.

45.4 Free energy, qualitatively

ΔG_{sys} is our working equation to determine spontaneity and spontaneity is decided by its sign. ΔG_{sys} also determines the kJ's which are available (theoretical maximum) for an exergonic process or the kJ's which must be paid (theoretical minimum) for an endergonic process. Ever since Chapter 18, we had worked with enthalpies of reaction but now we must understand that the enthalpy of reaction is only part of the picture. It is ΔG_{sys} which tells us the energy which is theoretically available to us as the result of an exergonic process and this number of kJ's may be less than or more than the kJ's from the enthalpy, ΔH_{sys} , alone. In fact, you can have an exergonic but endothermic process, and that process makes kJ's theoretically available to us although the system takes heat from the surroundings. Contrariwise, for an endergonic process, we must pay kJ's into the process and this amount may be more than ΔH_{sys} or we

may get away with paying less than ΔH_{sys} . All of these things depend on whether the $T \Delta S_{\text{sys}}$ part adds to the total or subtracts from the total. $T \Delta S_{\text{sys}}$ can even be greater than ΔH_{sys} and therefore it will have a greater contribution to ΔG_{sys} .

We have come a long way since Chapter 34 when we first saw that phases are the result of the balance of enthalpy versus entropy. That is now mathematically represented by the equation, $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$ and the specific point of balance is now given by $\Delta G_{\text{sys}} = 0$. For all phase changes, enthalpy and entropy oppose each other. For solutions, however, enthalpy and entropy can oppose each other or work together towards soluble or insoluble. We'll see some of this below when we do some calculations. Before getting to those calculations, let's work with some qualitative effects of the signs of ΔH_{sys} and ΔS_{sys} on the outcome of ΔG_{sys} . There are four possible variations on how ΔH_{sys} and ΔS_{sys} ultimately affect the sign of ΔG_{sys} . These apply to every reaction and process, not just phase changes and solubilities.

- VARIATION 1: The process is exothermic and system entropy increases.

The exothermic process gives J's to the surroundings and that increases S_{surr} . Also, S_{sys} increases. Thus, both favor spontaneity.

Arithmetically, ΔH_{sys} is negative and ΔS_{sys} is positive. Let's carry these signs into the free energy expression.

If you take a negative number

$$\begin{array}{r} (-) \\ \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}} \\ (+) \end{array}$$

and subtract a positive number

then you will always get a negative answer; ΔG_{sys} will always be negative. This Variation will always be exergonic (allowed).

- VARIATION 2: The process is endothermic and system entropy decreases.

The endothermic process takes in J's from the surroundings and this decreases S_{surr} . Also, S_{sys} decreases. Thus, both oppose spontaneity.

Arithmetically, ΔH_{sys} is positive and ΔS_{sys} is negative.

If you take a positive number

$$\begin{array}{r} (+) \\ \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}} \\ (-) \end{array}$$

and subtract a negative number

then you will always get a positive answer; ΔG_{sys} will always be positive. This Variation will always be endergonic (forbidden).

- VARIATION 3: The process is exothermic and system entropy decreases.

The exothermic process gives J's to the surroundings and this increases S_{surr} . On the other hand, S_{sys} decreases. These now oppose each other. This one's a toss-up.

For these, ΔH_{sys} is negative and ΔS_{sys} is negative.

If you take a negative number

$$\begin{array}{r} (-) \\ \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}} \\ (-) \end{array}$$

and subtract a negative number

then enthalpy and entropy oppose each other for the sign of ΔG_{sys} . Enthalpy favors exergonic; entropy favors endergonic.

For this Variation, sometimes you will get a negative answer and sometimes you will get a positive answer. Sometimes you can get zero, which is then equilibrium. All outcomes will depend on the actual numbers for ΔH_{sys} versus $T \Delta S_{\text{sys}}$.

- VARIATION 4: The process is endothermic and system entropy increases.

The endothermic process takes J's from the surroundings and decreases S_{surr} as a result. On the other hand, S_{sys} increases. These also oppose each other and we have another toss-up.

For these, ΔH_{sys} is positive and ΔS_{sys} is positive.

If you take a positive number

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}}$$

and subtract a positive number

then enthalpy and entropy again oppose each other for the sign of ΔG_{sys} . Enthalpy favors endergonic; entropy favors exergonic.

As in Variation 3, sometimes you will get a negative answer and sometimes you will get a positive answer. Sometimes you can get zero, which is then equilibrium. All outcomes will depend on the actual numbers for ΔH_{sys} versus $T \Delta S_{\text{sys}}$.

These four Variations cover all possibilities. There are no others. You'll need to sort through these and get comfortable with them. It may help to see how they apply to specific cases and we shall be getting to such examples later below and into the next Chapter.

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

By the way, I'll start dropping the subscript $_{\text{sys}}$ now that we have everything in terms of system. From now on, assume sys unless a specific subscript says otherwise.

Let's bring in some standards.

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

As usual, this applies to a reaction which begins at standard conditions and ends at standard conditions, and the middle doesn't matter. In other words, we can write the following.

$$\Delta H^\circ = H^\circ_{\text{final}} - H^\circ_{\text{initial}} \quad \Delta S^\circ = S^\circ_{\text{final}} - S^\circ_{\text{initial}} \quad \Delta G^\circ = G^\circ_{\text{final}} - G^\circ_{\text{initial}}$$

As a thermodynamic function, ΔG° has more parallel to ΔH° than to ΔS° . Let's take a look at some of the similarities and differences.

Units

Both ΔG° and ΔH° have units of kJ. ΔS° has units of J/K.

Products-minus-reactants

ΔS° for a reaction is calculated from products-minus-reactants using standard molar entropies, S° .

ΔH° for a reaction is calculated from products-minus-reactants but this uses standard enthalpies of formation, ΔH_f° . We need to use formation enthalpies because values for H° cannot be measured. All values of ΔH_f° are relative to standard reference element forms, for which ΔH_f° is set to zero.

ΔG° for a reaction is also calculated from products-minus-reactants and, like enthalpy, this uses formation values because values for G° cannot be measured. The standard free energy of formation is given by ΔG_f° . All values of ΔG_f° are also relative to standard reference element forms, for which ΔG_f° is set to zero.

Values for ΔG_f° for various substances are given in Appendix A along with values for ΔH_f° and S° . By the way, be sure to take numbers from the correct columns in that table or you'll mess up a calculation.

While we're here, let's revisit the reference element list as first presented in Section 19.2.

All Group 18 are monatomic(*g*).

Common diatomic gases: $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{F}_2(\text{g})$, $\text{Cl}_2(\text{g})$

$\text{C}(\text{graph})$, $\text{Br}_2(\text{l})$, $\text{I}_2(\text{s})$

$\text{Hg}(\text{l})$; all other metals(*s*)

Don't forget! For all of the standard elemental reference forms, $\Delta H_f^\circ = 0$ and $\Delta G_f^\circ = 0$, but S° is some positive number. In addition, we assign $\text{H}^+(\text{aq})$ as the standard reference ion for all three functions and values for all ions in aqueous solution are relative to these. Thus for $\text{H}^+(\text{aq})$, ΔH_f° is set to zero, ΔG_f° is set to zero, and even S° is set to zero. $\text{H}^+(\text{aq})$ is the only thing that gets zero for all three.

45.5 Free energy, quantitatively

Free energy is our working manifestation of the law. It tells us can and cannot. It tells us how many kJ's can be made available to us during the course of a reaction. These are the energies which are

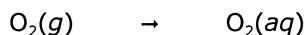
available to power your cells, your body, your house, your city, your Earth and beyond. Or, these are the energies which we must pay into a system if a reaction cannot happen by itself. And then there's zero, that magical condition of balance.

We now begin to put numbers to free energy.

As mentioned, there are two ways to calculate ΔG° for any reaction. You can calculate it from ΔH° and ΔS° via $\Delta H^\circ - T \Delta S^\circ$ or you can calculate it via products minus reactants using ΔG_f° . Let's look at some examples.

We'll start with a somewhat simple process: dissolving $O_2(g)$ in water. For this, we'll find each of $\Delta H_{\text{soln}}^\circ$, $\Delta S_{\text{soln}}^\circ$ and $\Delta G_{\text{soln}}^\circ$.

Start with an equation.



For $\Delta H_{\text{soln}}^\circ$, you need ΔH_f° values from Appendix A, at least for $O_2(aq)$.

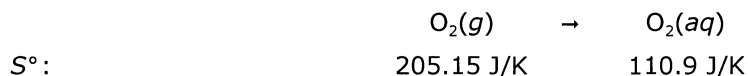


Now, products minus reactants:

$$\Delta H_{\text{soln}}^\circ = 1(-11.7 \text{ kJ}) - 1(0 \text{ kJ}) = -11.7 \text{ kJ}$$

This calculation says dissolving $O_2(g)$ into water at standard conditions is exothermic.

For $\Delta S_{\text{soln}}^\circ$, you need S° values from Appendix A.



Now, do products minus reactants:

$$\Delta S_{\text{soln}}^\circ = 1(110.9 \text{ J/K}) - 1(205.15 \text{ J/K}) = -94.2 \text{ J/K}$$

This was one of the examples cited in Chapter 44. Again, dissolving $O_2(g)$ into water at standard conditions is very disfavored by entropy.

From these first two calculations, we see that the dissolution of O_2 into water is exothermic which favors exergonic, but the process has a negative $\Delta S_{\text{soln}}^\circ$ which favors endergonic. This is Variation 3. Put it all together.

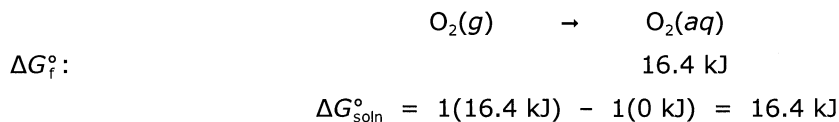
$$\begin{aligned} \Delta G_{\text{soln}}^\circ &= \Delta H_{\text{soln}}^\circ - T \Delta S_{\text{soln}}^\circ \\ \Delta G_{\text{soln}}^\circ &= -11.7 \text{ kJ} - (298.15 \text{ K})(-94.2 \text{ J/K}) = -11.7 \text{ kJ} - (-28.1 \text{ kJ}) = 16.4 \text{ kJ} \end{aligned}$$

In the end, $\Delta G_{\text{soln}}^\circ$ is positive. The favorable $\Delta H_{\text{soln}}^\circ$ is outweighed by the unfavorable $T \Delta S_{\text{soln}}^\circ$ term. The process is doomed. Dissolving cannot happen by itself at standard conditions. If you look back at Section 40.2, you'll see how we approached this process qualitatively.

By the way, here's a pointer for doing these calculations. Typically, ΔH° is in kJ and ΔS° is in J/K. Multiplying ΔS° by T gives J. Be sure to decimal shift this value by three places to get it into kJ before combining it with ΔH° . That is shown above as -28.1 kJ for $T \Delta S_{\text{soln}}^\circ$.

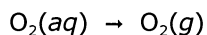
Let's check out the other way to find ΔG° .

We need values of ΔG_f° from Appendix A. We need to look up the value for $O_2(aq)$. If you want to look up the value for $O_2(g)$ then go ahead but, when you find it, you'll see why you didn't have to.



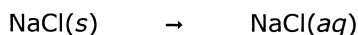
This value for $\Delta G_{\text{soln}}^\circ$ agrees exactly with the value found upstairs from $\Delta H_{\text{soln}}^\circ - T \Delta S_{\text{soln}}^\circ$, but it's not unusual if the two ways give a very slightly different number. Be aware of that.

Dissolving $O_2(g)$ into water at standard conditions is forbidden. However, the reverse reaction,



can happen by itself. This is exergonic, with $\Delta G^\circ = -16.4$ kJ.

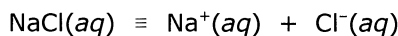
Let's try dissolving NaCl into water. Find $\Delta H_{\text{soln}}^\circ$, $\Delta S_{\text{soln}}^\circ$ and $\Delta G_{\text{soln}}^\circ$.



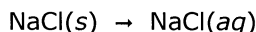
For $\Delta H_{\text{soln}}^\circ$, you need ΔH_f° values.

$$\Delta H_f^\circ: \quad \quad \quad -411.12 \text{ kJ} \quad \quad \quad -407.28 \text{ kJ}$$

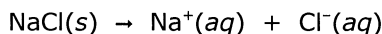
If you look for the -407.28 in Appendix A, you won't find it. Assuming full dissociation, then



and this applies for cases of full dissociation as was shown for entropy in Section 44.2. Thus, the equation



is equivalent to



and you will find the values for $\text{Na}^+(aq)$ and for $\text{Cl}^-(aq)$ in Appendix A. You can use the individual ion values or their sum (-407.28 kJ) for products minus reactants in order to get the enthalpy of solution. Here it is using the sum value.

$$\Delta H_{\text{soln}}^\circ = 1(-407.28 \text{ kJ}) - 1(-411.12 \text{ kJ}) = 3.84 \text{ kJ}$$

Dissolving $\text{NaCl}(g)$ into water at standard conditions is endothermic. Interestingly, we derived this same $\Delta H_{\text{soln}}^\circ$ in Section 39.4 using $\Delta H_{\text{latt}}^\circ + \Delta H_{\text{hydr}}^\circ$!

$\Delta S_{\text{soln}}^\circ$ was shown in Section 44.2.

$$\Delta S_{\text{soln}}^\circ = 1(115.5 \text{ J/K}) - 1(72.12 \text{ J/K}) = 43.4 \text{ J/K}$$

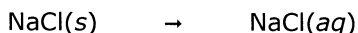
Overall, endothermic opposes dissolving; positive $\Delta S_{\text{soln}}^\circ$ favors dissolving. This is Variation 4. Now, put it together.

$$\Delta G_{\text{soln}}^\circ = \Delta H_{\text{soln}}^\circ - T \Delta S_{\text{soln}}^\circ$$

$$\Delta G_{\text{soln}}^\circ = 3.84 \text{ kJ} - (298.15 \text{ K})(43.4 \text{ J/K}) = 3.84 \text{ kJ} - 12.9 \text{ kJ} = -9.1 \text{ kJ}$$

The process is exergonic. The system takes up 3.84 kJ from the surroundings in order for this process to happen. In losing that amount of thermal energy, the surroundings lose entropy. That's bad. However, that loss is more than offset by the increase in entropy of the system. That's good. Thus, total S_{univ}° increases overall. The process can happen by itself under the given (standard) conditions.

Let's do $\Delta G_{\text{soln}}^\circ$ from ΔG_f° .

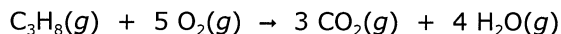


$$\Delta G_f^\circ: \quad \quad \quad -384.02 \text{ kJ} \quad \quad \quad -393.13 \text{ kJ}$$

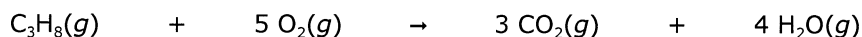
$$\Delta G_{\text{soln}}^\circ = 1(-393.13 \text{ kJ}) - 1(-384.02 \text{ kJ}) = -9.11 \text{ kJ}$$

It's the same answer although we did get an extra sigfig by this method. Both methods and both answers are correct.

These are very simple examples. Let's do something more complicated. Let's do the combustion of propane, $\text{C}_3\text{H}_8(g)$.



In Chapter 19 we calculated the value of $\Delta H_{\text{comb}}^\circ$ for liquid phase water as product. Now I want to use gas phase water, so we need to calculate $\Delta H_{\text{comb}}^\circ$ for this outcome.



$$\Delta H_f^\circ: \quad -104.70 \text{ kJ} \quad \quad \quad 0 \text{ kJ} \quad \quad \quad -393.52 \text{ kJ} \quad \quad \quad -241.83 \text{ kJ}$$

$$\Delta H_{\text{comb}}^\circ = 3(-393.52 \text{ kJ}) + 4(-241.83 \text{ kJ}) - 1(-104.70 \text{ kJ}) - 5(0 \text{ kJ}) = -2,043.18 \text{ kJ}$$

For the entropy part, you did $\Delta S_{\text{comb}}^\circ$ at the end of Chapter 44 and you (should have) obtained $\Delta S_{\text{comb}}^\circ = 100.66 \text{ J/K}$. Overall, the reaction is exothermic and entropy increases. Both favor spontaneity. This is Variation 1. Now, put them together.

$$\Delta G_{\text{comb}}^\circ = \Delta H_{\text{comb}}^\circ - T \Delta S_{\text{comb}}^\circ$$

$$\Delta G_{\text{comb}}^{\circ} = -2,043.18 \text{ kJ} - (298.15 \text{ K})(100.66 \text{ J/K}) = -2,043.18 \text{ kJ} - 30.012 \text{ kJ} = -2,073.19 \text{ kJ}$$

The combustion is exergonic. The very large energy release to the surroundings increases S_{sur}° ; additionally, S_{sys}° increases. In fact, this reaction is big time exergonic. That's typical of the compounds which society uses for fuels. Fuels are typically chosen to provide a very large amount of available energy and most of that comes from the enthalpy term.

Your turn.

Example 1. Find $\Delta G_{\text{comb}}^{\circ}$ for propane from ΔG_f° values.

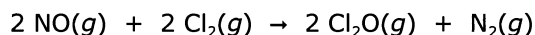
Set up products minus reactants.

$$\begin{array}{ccccccc} \text{C}_3\text{H}_8(g) & + & 5 \text{ O}_2(g) & \rightarrow & 3 \text{ CO}_2(g) & + & 4 \text{ H}_2\text{O}(g) \\ \Delta G_f^{\circ}: & -24.31 \text{ kJ} & 0 \text{ kJ} & & -394.39 \text{ kJ} & & -228.58 \text{ kJ} \\ \Delta G_{\text{comb}}^{\circ} & = & \text{_____} (\text{_____ kJ}) & + & \text{_____} (\text{_____ kJ}) & - & \text{_____} (\text{_____ kJ}) \\ & = & \text{_____} & & & & \text{J/K} \end{array}$$

Your answer is a tad smidgeon different from the one above, but both are correct.

Alright, one more example.

Example 2. Consider the following reaction.



Find ΔH° , ΔS° and then ΔG° from those values. In addition, find ΔG° directly from values for ΔG_f° . Is the reaction exergonic or endergonic?

Here are some numbers.

$$\begin{array}{ccccccc} 2 \text{ NO}(g) & + & 2 \text{ Cl}_2(g) & \rightarrow & 2 \text{ Cl}_2\text{O}(g) & + & \text{ N}_2(g) \\ \Delta H_f^{\circ}: & 90.29 \text{ kJ} & 0 \text{ kJ} & & 81.00 \text{ kJ} & & 0 \text{ kJ} \\ S^{\circ}: & 210.76 \text{ J/K} & 223.08 \text{ J/K} & & 271.72 \text{ J/K} & & 191.61 \text{ J/K} \end{array}$$

Do ΔH° :

Do ΔS° :

Do ΔG° from ΔH° and ΔS° :

The reaction is exothermic and S_{sys}° decreases. (What's the biggest reason for the negative $\Delta S_{\text{sys}}^{\circ}$?) This is Variation 3. Enthalpy and entropy oppose each other, and the reaction comes out endergonic. This reaction cannot happen by itself at standard conditions.

OK, now do ΔG° from ΔG_f° .

$$\begin{array}{ccccccc} 2 \text{ NO}(g) & + & 2 \text{ Cl}_2(g) & \rightarrow & 2 \text{ Cl}_2\text{O}(g) & + & \text{ N}_2(g) \\ \Delta G_f^{\circ}: & 86.60 \text{ kJ} & 0 \text{ kJ} & & 97.08 \text{ kJ} & & 0 \text{ kJ} \end{array}$$

The two methods give the same answer for this Example.

We have now completed several illustrations which show the importance of free energy and its link to total entropy. These kinds of calculations are straightforward but that belies the scope of their impact.

There are very many things that ΔG° touches upon, some of which we shall see in the next Chapter and then into later Chapters.

Problems

- True or false.
 - For equilibrium, $\Delta S_{\text{univ}} = 0$.
 - An exergonic process has a positive ΔS_{univ} .
 - An endergonic process cannot happen by itself under the given conditions.
 - All endothermic reactions are spontaneous.
 - An allowed reaction has a negative ΔG .
 - The standard reference elemental form of bromine is the diatomic gas.
- True or false.
 - The standard reference elemental form for carbon is diamond.
 - The sign of ΔG gives the allowed direction for a process.
 - At equilibrium, ΔG equals zero.
 - All reactions with $\Delta S_{\text{surr}} < 0$ are spontaneous.
 - In order for a reaction in a system to be endothermic and exergonic, $\Delta S_{\text{sys}}^\circ$ must be a positive value.
 - If a process is exergonic, then S_{universe} increases.
- Which of the following substances have $\Delta G_f^\circ = 0$?
 Ne(g) H⁺(aq) I₂(g) Cl⁻(aq) Br₂(g) Al(s)
- Consider the following reaction.

$$\text{CS}_2(g) + 3 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{SO}_2(g)$$
 - Find ΔH° (in kJ) for this reaction.
 - Find ΔS° (in J/K) for this reaction.
 - Using the above values, what is ΔG° (in kJ) for this reaction at 298.15 K?
- Consider the following reaction.

$$\text{Cl}_2\text{O}(g) + 2 \text{H}_2(g) \rightarrow 2 \text{HCl}(g) + \text{H}_2\text{O}(g)$$
 - Find ΔH° (in kJ) for this reaction.
 - Find ΔS° (in J/K) for this reaction.
 - Using the above values, what is ΔG° (in kJ) for this reaction at 298.15 K?
- Consider the following reaction.

$$\text{PCl}_5(g) + 4 \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{PO}_4(aq) + 5 \text{HCl}(aq)$$
 - What is ΔH° (in kJ) for this reaction?
 - What is ΔS° (in J/K) for this reaction?
 - Using the above values, what is ΔG° (in kJ) for this reaction at 298.15 K?
- Which of the conditions a - d below are always exergonic?
 - Exothermic, positive ΔS_{sys}

- b. Endothermic, positive ΔS_{sys}
 - c. Exothermic, negative ΔS_{sys}
 - d. Endothermic, negative ΔS_{sys}
8. Consider the following reaction.
- $$\text{PCl}_3(g) + 3 \text{H}_2(g) \rightarrow \text{PH}_3(g) + 3 \text{HCl}(g)$$
- Using free energies of formation, what is ΔG° (in kJ) for this reaction?
9. Consider the following reaction.
- $$2 \text{PbO}_2(s) + 4 \text{H}^+(aq) \rightarrow 2 \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$$
- Using free energies of formation, what is ΔG° (in kJ) for this reaction?
10. The combustion of hydrazine, $\text{N}_2\text{H}_4(l)$, with $\text{O}_2(g)$ produces $\text{N}_2(g)$ and $\text{H}_2\text{O}(g)$. Using free energies of formation, what is ΔG° (in kJ) for this reaction?