I am going to continue our blitz through a review of thermodynamics. And we are going to start, right now, talking about spontaneous change.

And you all know what spontaneous change means.

It means some change that occurs without intervention.

Spontaneous change has a directionality to it.

For example, if you put a rock at the top of a hill and you let go, it rolls down, it doesn't roll up. If you put a warm body next to a hot body, the heat flows from the hot body to the cold body, and not the other way. If you, for example, have a bulb of gas here and a stop-cock and an empty bulb, you open the stop-cock, that gas flows from the high pressure region to the low pressure region, and it does not go the other way.

However, spontaneous change does not have to be fast.

You know that if you take a bottle of ketchup, when it used to be a glass bottle that you couldn't squeeze, and you turn it over, that ketchup has a spontaneous tendency to flow out. But it does not have to be fast. What is, in chemical reactions, the key to spontaneity? Is it the exothermicity?

Well, certainly iron rusts. You don't have to do anything to make it rust. A very exothermic reaction.

Delta H is about 824 kilojoules per mole.

If you have an acidic stomach and you then ingest something that is a little bit more basic, well, this reaction goes.

It neutralizes that acid, also an exothermic reaction.

You did not have to do anything other than drink the more basic solution. This reaction, here, this hydrolysis of ATP to ADP, adenosine diphosphate, -- -- proceeds in every cell of your body, and you don't have to do anything to make that go.

That is an exothermic reaction. But what about an endothermic reaction? How about this reaction?

This is ammonium nitrate dissolving in water to make ammonium ions and nitrate ions. The delta H for this reaction is positive, plus 25.7 kilojoules per mole.

It is an endothermic reaction. Is this reaction spontaneous?

Well, yes. We are going to do an experiment anyway. And the experiment we are going to do is, you are going to be given one of these cold packs.

And the TAs can start distributing them.

What you have to do is find the little pouch inside the cold pack that contains the water. You have to press on that, allowing the water to disperse in the material, and you will see if the reaction goes.

If it goes, that cold pack better get cold because this is an endothermic reaction. It is going to remove some heat from the environment. Some of you will get hot packs, and we will see if that is spontaneous.

Is an endothermic reaction spontaneous?

Yes. Is an exothermic reaction spontaneous? Yes, right.

Is delta H the key to spontaneity?

No. What is?

Delta G, right. So, delta G is the key to spontaneity. You already know that when delta G is negative, you have a spontaneous reaction. When delta G is positive, you have a non-spontaneous reaction.

And very importantly, when delta G is zero, that is when you are at equilibrium.

That is what we are going to be talking about in just a few minutes, when delta G is equal to zero.

These are the conditions, of course, for constant temperature and pressure. Delta S, in this expression for delta G, is the change in the entropy.

It is a measure of disorder. When delta S is positive, we have an increase in the disorder.

When delta S is negative, we have a decrease in the disorder. Where do these conditions come from? You are going to talk about that in exquisite detail in 5.60, but I want to give you a physical understanding for what delta G is.

And that is this. Suppose you have an exothermic reaction. It turns out that not all of that exothermicity, not all of that enthalpy, can be released to the outside world to do useful work.

Some of that enthalpy is actually caught up in the product molecules, or can be caught up in the product molecules. Some of that enthalpy gets stuck in the product molecules. It gets stuck in the vibrations and rotations of the product molecules in the internal degrees of freedom. It is that energy that is not available to do useful work. For some exothermic reactions, here, the amount of energy that is available to do useful work is something smaller than delta H.

It is delta H minus T delta S, where T delta S, then, is a measure of how much of that enthalpy is stuck in the internal degrees of freedom of the molecule.

And so, this delta G is called the free energy because this is the amount of energy that is free to do useful work.

That is what delta G is. For example, if you go home and turn on your gas stove, oxidize some methane, burn some natural gas to heat up the water for your pasta, that delta H is very negative. But let's now calculate delta G. Well, to do that, we need to know what delta S is.

Delta S, I will show you in just a moment, is the change in the entropy. We can calculate that.

But knowing delta S then, we can plug in the delta H and the temperature. What we find is that delta G here is less negative than delta H.

Not all of this enthalpy, not all of that energy is available to the outside world to do useful work.

Some of it, in this reaction, gets trapped or caught in the internal degrees of freedom of a molecule.

And it is not available to do that useful work.

Delta G, in this case, is less negative than delta H.

But let's take the eat, breathe, exhale, pee reaction. The oxidation of glucose, going on in every cell of your body, this reaction also very exothermic. Let's calculate delta G for this reaction. Well, first of all, we need delta S. From that, we can calculate delta G. And, in this case, what do you see? In this case, you see that delta G is more negative than delta H.

In this exothermic reaction, we are getting back all of the enthalpy and then some. We are getting back even more.

And that extra energy is coming from the energy that is tied up in the internal degrees of freedom of the reactants.

In this reaction, here, delta S is positive.

We are increasing the disorder. If we increase the disorder, there are fewer ways to tie up energy in the internal degrees of freedom of the molecule. When we increase the disorder, that is what happens. And so, your body has figured out how to get back all of that delta H, and then some.

We are getting that energy out that is locked up in the reactants, in the internal degrees of freedom of the reactants. That is a physical feeling, there, for what delta G is. Entropy for a reaction.

The entropy is calculated from the absolute entropies of the products and the reactants. And so, what you need are the absolute entropies for each one of the products multiplied by the appropriate stoichiometric number.

You sum them all up. And you do the same then for the reactants, the absolute entropy of each one of the reactants multiplied by that stoichiometric number.

Sum them up. Subtract it.

That is the entropy change for the reaction.

Now, one thing I do want to point out is that in the case of entropies, here, these are absolute entropies.

That is rather unusual in thermodynamics.

In thermodynamics usually we look at changes in energies, but here we are talking about absolute entropies.

That is a consequence of the third law of thermodynamics.

You will see how that arises again in 5.60, but right now we are going to use it to calculate the entropy for a reaction. And some reactions here are completely entropy-driven. For example, if you melt ice, this is an endothermic reaction, 6.95 kilojoules per mole.

In going from solid water to liquid water, you have to put energy into the system to do that.

But you know that this reaction occurs spontaneously.

If I had a cube of ice here, it would melt.

This reaction is entropy-driven.

Why? Let's look at it.

Let's calculate delta S for that reaction.

You need the absolutely entropy for water in the liquid phase, that is the product, minus the absolute entropy for water in the solid phase. The difference between the two is positive. We have increased the disorder.

There are less ways to tie up energy in liquid water than there are in solid water, in ice.

And that fact is going to make this reaction then spontaneous, 6.95 positive for delta H minus T delta S.

This term, T delta S, now is larger in absolute magnitude. Therefore, delta G is negative.

This reaction is spontaneous. It is certainly entropy-driven.

The other concept I want to talk about is the free energy of formation, which is analogous to what we talked about last time, the enthalpy of formation. The free energy of formation is the free energy for a reaction that forms one mole of a compound from the elements in their most stable form in the standard state. And our standard state is one bar. The free energy of formation, here, is tabulated like the heats of formation.

You can find tables of free energy and enthalpy of formation for all molecules. However, unlike the enthalpy of formation, the free energy of formation can also be calculated easily by you, which is the following, if you know the enthalpy of formation for some reaction.

Or, for the reaction that defines the enthalpy of formation. And if you know what the entropy change is for that reaction that defines the enthalpy of formation, then you can calculate the free energy here of formation. You have two choices in the case of the free energy of formation.

You can look it up. Or, if you know what delta H sub f and delta S are for the reaction, that defines the free energy of formation or the enthalpy of formation. You can calculate the free energy of formation, here.

Here is a reaction that forms one mole of CO two.

And the delta G for this reaction is minus 394 kilojoules per mole. The delta G for this reaction is defined as the free energy of formation for CO two.

It is so because we are forming one mole of this molecule from the elements in their most stable form in the standard state. The most stable form of the element carbon is graphite. The most stable form of the element oxygen is molecular oxygen.

But what is important about the free energy of formation, here, is that it is a measure of a compound stability relative to decomposition to its elements.

For example, the free energy of formation of carbon dioxide is negative. What that means is CO two is thermodynamically stable relative to decomposition into its elements. Because delta G for this reaction is written as negative. The reaction is spontaneous in this direction. It is not spontaneous in the reverse direction. That is, the decomposition of CO two to its elements is not a spontaneous process.

Therefore, we say that CO two is thermodynamically stable relative to decomposition into its elements.

If you have a free energy of formation for a molecule that is negative, it is thermodynamically stable, but if you have a free energy of formation that is positive, then that compound is not thermodynamically stable relative to decomposition to its elements.

For example, let's look at benzene.

Here is a reaction that forms one mole of liquid benzene from the elements in their most stable form in the standard state, graphite and molecular hydrogen.

The free energy of formation for this benzene is positive kilojoules per mole. That means that this forward reaction, as written, is not spontaneous.

However, the reverse reaction is spontaneous because delta G is minus 124 kilojoules per mole.

And so we say benzene, here, is thermodynamically unstable relative to its elements.

But, even though you might have a reaction, here, that is spontaneous, that is the reverse reaction.

You have a delta G formation that is positive, meaning the reverse reaction is spontaneous.

Even though that reverse reaction may be spontaneous, it also could be very, very slow.

When was the last time you saw a pint of benzene decompose into graphite and hydrogen? You haven't seen that.

I haven't seen that and I am a lot older.

What this means is that even though you might have a thermodynamic tendency to compose, it does not mean that it is going to happen because there is a question of the rate of the chemical reaction. We have two different terms to describe the thermodynamic tendency and then the kinetic tendency, and these terms are the following.

We call the molecules stable or unstable when we are referring to the thermodynamic tendency. That is when we are referring to delta G or the free energy of formation.

If it is negative, the molecule is stable.

If it is positive, the molecule is unstable relative to decomposition. However, we also have to consider the rates. And we have another term to describe the rates. And that is labile and non-labile. If a molecule is non-labile, what that means is that the rate, at which the thermodynamic tendency is realized, is very, very slow.

Benzene, for example, is thermodynamically unstable relative to decomposition into its elements, carbon and hydrogen, but it is non-labile.

The rate at which that reaction happens is just too slow to be of any practical interest to you.

However, if this decomposition reaction occurred very readily, then we would call that molecule labile.

That is, the rate of the decomposition is something that is going to affect your ability to handle that particular compound or that molecule. Like the enthalpy of formation, the free energy of formation can also be zero.

Last time, we talked about how the enthalpy of formation for hydrogen, oxygen, chlorine, xenon, all of that, had zero enthalpy of formation.

Well, all of these molecules have zero free energy of formation because they are all in the most stable form already, in the standard state. The free energy of formation of bromine liquid and mercury liquid is zero. Because they are in the most stable form at the standard state.

The free energy of formation of carbon in the form of graphite, sodium solid, iron solid, iodine solid.

Those free energies of formation are all equal to zero, but the free energy of formation here of bromine in the gas phase is not equal to zero. Because bromine gas is not the most stable form in our standard state.

Liquid bromine is, so it is going to take energy to produce bromine gas. So Delta G of formation is not going to be zero. Likewise, the free energy of formation of diamond is not equal to zero.

Because carbon, in the form of diamond, is not the most stable form of carbon.

Graphite is. This is going to take energy to form that configuration of carbon.

So free energies of formation are very important in terms of understanding the thermodynamic stability of molecules.

Just a review, here.

If you want to calculate delta G for a reaction, what can you do? You can take the free energy of formation for each one of the products, multiply it by the appropriate stoichiometric number, since those free energies of formation are given per mole, add them all up, and then do the same thing for the reactants.

Free energies of formation for each of the reactants.

Stoichiometric number. Add them all up.

Subtract the two. That is the delta G for your chemical reaction. Like delta H for the chemical reaction, which you calculated from the differences in the heats of formation, the products and reactants, note that this is products minus reactants.

This is different from when you calculate delta H, for example, from bond enthalpies.

That was reactants minus products.

Something to remember. But again, in the case of delta G, we can calculate it from knowing the free energies of formation of the reactants and the products.

But we can also calculate it from this expression.

If, for example, you know the enthalpy change for a reaction and you know the entropy change for a reaction, you can calculate the free energy change from these two quantities. You have two choices to calculate the free energy change of some chemical reaction, depending on what information is known or is given to you.

Now, I want to talk kind of briefly about controlling the spontaneity of a chemical reaction.

And, to do so, I am going to talk about this molecule, which is sodium bicarbonate.

Sodium bicarbonate is better known as baking soda.

It is what you put into some batter of soft baked goods that you want to make. What happens is that the sodium bicarbonate decomposes and two of the products are gases, CO two and water. And so, in your batter, what you get are these bubbles of CO two and water.

And what happens is that the dough starts to harden around these bubbles. And then, of course, eventually, the CO2 and water leave, are completely driven off, but what that leaves behind in the batter is a very porous structure, so porous that after you remove it from the oven you can actually put your teeth into it.

Have you ever left out the baking soda in some soft baked goods? You cannot get your teeth into it, right? So, this is an important reaction. But this is a reaction, here, that is very endothermic. It does increase in the entropy, but at room temperature, this reaction has a positive delta G. This reaction does not proceed.

It is non-spontaneous in the forward direction, as written. And that is good because you do not want this reaction to start when your batter is still on your kitchen counter. You want it to start when it is in the oven. What happens as we raise the temperature, here? For the purposes of what we are going to do, we have the same delta H and delta S.

But now, when we calculate delta G, the temperature, here, is going to be our baking temperature of 350 degrees Fahrenheit. And now, what you see is delta G is negative, minus 14 kilojoules per mole.

All of a sudden, this reaction became spontaneous. And we made it spontaneous simply by increasing the absolute magnitude of T delta S.

We increased it by increasing the temperature, in this case. We made it spontaneous by raising the temperature. For some reactions, we can do that. We can find a temperature at which the reaction will be spontaneous.

Let's look at the particular conditions.

Delta G is a linear function of the temperature, so let me draw that for this particular case, for the sodium bicarbonate decomposition.

The slope of this line for this reaction is, of course, minus delta S. The intercept is delta H.

And now, let me just draw a zero here.

What I want you to notice is that there is some temperature that I am going to call T star.

There is some temperature at which the sign of delta G changes. You see that below T star, delta G is positive. Below those temperatures, such as room temperature for the sodium bicarbonate decomposition, delta G is positive.

We have a non-spontaneous reaction.

Above some temperature delta G has become negative.

We have a spontaneous reaction. We can calculate the value of this T star, where the spontaneity switches, by setting delta G nought equal to zero and then solving for T star. Let's do that.

I rearrange this to give me T star is equal to delta H over delta S. For this reaction, I know the values of delta H and delta S.

And for this reaction that value of T star is 406 Kelvin.

So, your oven has to be higher in temperature than 406 Kelvin if you want to make some baked goods that you can put your teeth into. For some reaction, in this particular case here that is endothermic, delta H greater than zero, in which case we have an increase in entropy, that reaction is spontaneous whenever the temperature is above some temperature T star.

But we also have reactions which are exothermic, delta H less than zero, and reactions in which the entropy decreases. Delta S is less than zero.

And I have plotted that line here, delta G versus T.

For the opposite condition, we have the opposite slope because delta S has changed sign.

In this case, the reaction will be spontaneous whenever the temperature is below some temperature T star. And you can see that by looking at the relative signs in this expression.

If delta H is less than zero up here, then we have a negative quantity right here. And, since delta S is less than zero, we have minus times a minus, which is a plus.

This term here is positive, this term is negative, and so this positive term better not be in absolute value very much larger than delta H here.

If it is, then we are going to have a positive delta G, but if this term is small compared to the absolute value of delta H, then we will have a spontaneous reaction at low temperatures. So, you want to keep this term small. That is why it is spontaneous when T is less than T star. But we can also have reactions that are exothermic and reactions in which the entropy increases. In this case, you have the best of all worlds.

In this case, this reaction is spontaneous at all temperatures. You cannot adjust the spontaneity of this reaction by temperature.

This is always going to be negative.

Delta H is negative here, minus T delta S.

This is going to be minus a positive number.

A negative minus a positive number is always a negative number, always spontaneous. And then, finally, we can have a condition where we have an endothermic reaction, delta H is greater than zero, and where the entropy decreases, delta S is less than zero.

In this case, the reaction is never spontaneous, no matter what temperature you do.

You cannot adjust that non-spontaneity with temperature. Delta H, you can see that, is going to be positive. And since delta S is negative, we have a minus times a minus, that is positive, delta G is positive at all temperatures.

So we have failed to adjust the spontaneity with temperature for some reactions that are endothermic and in which the entropy decreases.

What we have been talking about are values of delta G that are standard state. We have been talking about delta G nought, one bar pressure.

That is what we have been talking about.

What that means is that the delta G nought for any reaction means that we have one atmosphere each of the products and the reactants. That is what delta G nought means. That our famous reaction here, argon-boron, argon plus boron going to carbon plus deuterium. Let's take this reaction.

When I give you a delta G nought for this famous reaction, what that means is that that is the delta G nought when the partial pressure of the reactant A is one bar, and the partial pressure of reactant B, is one bar and the partial pressure of product C is one bar, and the partial pressure of product D is one bar.

That does not seem real useful, because say you were going to start a reaction and you just start it even with one bar of A and one bar of B, this is not the delta G under those particular conditions. We have to be able to calculate delta G under any conditions. Not just our standard state conditions. And that is what we are going to do with this expression. We are going to be able to calculate a delta G at any time during a reaction.

We can stop a reaction, and we can measure the partial pressures of the reactants and the products present, and we can get from that, then, a delta G for a reaction at that particular point. That is what we are going to do, here. What have I got written here?

I have delta G is equal to this delta G nought, the standard state delta G, plus RT ln of the partial pressure of product C over some reference pressure raised to the appropriate stoichiometric number, times the partial pressure of the other reactant, divided by some reference pressure raised to the appropriate stoichiometric number. And that is all over the product of the partial pressure of A over that reference pressure, raised to the appropriate stoichiometric number, times the same for reactant B.

What this ratio here of partial pressures is, or what it is called, is the reaction quotient, Q. It is the ratio of the partial pressures present during any time during the reaction.

Not necessarily at equilibrium -- at any time during the reaction. That is what Q is here.

And so in this way, with this expression, we are going to be able to calculate what delta G is for the reaction at any time outside of this special standard state of one bar pressure for each one of the reactants, one bar partial pressure for each one of the products.

Where this expression comes from is, again, discussed in exquisite detail in 5.60.

You will see where it comes from later, but right now we are going to use it to calculate delta G at any time during the reaction. But now let me point out that our reference pressure right here is one bar.

What I am going to do is substitute a one in here for each one of the reference pressures, so that my reaction quotient is going to look like this.

And I did not put in the bars because what you are going to do is put in the pressures in bars. And then, the reaction quotient will be just fine. You have to use bar pressure here, since that is our standard state.

That is our reference pressure. Now, keep this in mind.

This is important. We are going to use this again in just a moment. Let's start talking about the equilibrium constant. Here is our famous A plus B going to C plus D reaction.

We already said if delta G, for this reaction as written is negative, then that forward reaction is spontaneous.

If delta G for that reaction is positive for the reaction as written, what that means is then, the reverse reaction is spontaneous. And now, very importantly, if delta G is zero, then we are at chemical equilibrium. Notice this is delta G equal to zero. This is not delta G nought equal to zero. A big difference here.

This is delta G equal to zero. Then, we are at equilibrium.

What I am going to do is I am going to bring back my expression that allowed me to calculate delta G at any arbitrary pressures of the reactants and the products.

And I just said that equilibrium, here, is defined by delta G being equal to zero, so I am going to plug in a zero right in there.

If that is the case, then I am going to rearrange this equation. I am going to bring delta G over to the other side, and that is what I do here on the next slide. I have delta G nought is equal to minus RT ln of this reaction quotient.

Now, we have a special condition here. And that is when delta G is equal to zero, when we are at thermodynamic equilibrium this reaction quotient has a special name.

That special name is the equilibrium constant, K. This reaction quotient is equal to the thermodynamic equilibrium constant.

And it is so only when delta G is equal to zero.

Not delta G nought equal to zero.

We get the equation, delta G nought is equal to minus RT ln of K.

That is where this particular expression comes from.

So, the reaction quotient is equal to K when we are at thermodynamic equilibrium. Now what we are going to do is set up some equations here that are going to allow us to quickly tell when our reaction is at equilibrium.

We are going to compare Q to K. Let's do that.

Here is that general expression I had that allowed me to calculate delta G at any arbitrary pressures of the reactants and the products. Here is the expression delta G nought at equilibrium, delta G nought equal minus RT ln of K.

What I am going to do is substitute this delta G nought into here right in there. Let me do that.

I am just going to plug it right in.

So, I have minus RT ln of K plus RT ln of Q.

Now I have the difference between two logs. The difference between two logs is the log of the quotient of those arguments of the logs.

So, delta G then is RT times ln of Q over K.

Remember what Q is?

It is this ratio of instantaneous partial pressures.

If we have a reaction running and we somehow measure the partial pressures at some time, and we calculate the reaction quotient from that and then we find that Q is less than K, the equilibrium constant, what that means is that we have fewer products present than equilibrium says we should have -- -- because Q is less than K.

If that is the case, then what is going to happen is that the reaction is going to proceed in the forward direction in order to make more products, so that Q can get to the point of being equal to K. You can also see that up here.

When Q is less than K, we had the log of a number that is going to be less than one. The log of a number less than one is a negative number. When Q is equal to K, delta G is going to be negative, meaning, the reaction as written is spontaneous in the forward direction. That is what our equilibrium says. It wants to make more products.

On the other hand, if we have Q greater than K, that says we have too many products compared to what equilibrium says we should have. And, of course, then the reaction is going to run in the reverse direction.

It is going to try to use up those products and make more reactant. You can also see that by this expression. When Q is greater than K, we are going to have a log of a number that is greater than one, that is going to be positive. If delta G is positive in the forward direction for the reaction as written, then it is the reverse reaction that is going to be spontaneous.

Another way to look at it is shown here.

Suppose we are in a situation where Q is less than K.

I am plotting here Q as a function of the time in the reaction, and I am starting out here at T equals zero and Q is less than K. If Q is less than K, it means that we have fewer products than what equilibrium tells us we should have. The reaction is going to proceed in the forward direction, so that Q will increase to the value of K, so that we can attain equilibrium. On the other hand, if we have a situation where we start a reaction, but Q is greater than K, in that case, we started the reaction by putting all the products in instead of the reactants. When Q is greater than K, it says we have more products than equilibrium says we should have. What is going to happen is that the reverse reaction is going to proceed.

It is going to try to use up those products, so that we attain this ratio given by the equilibrium constant. That is how we are going to use Q, compare it to K to determine whether or not we are at chemical equilibrium. Professor Cummins will be here on Wednesday. I will see you later in the week.