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PROFESSOR NELSON: So, over the last few lectures we've worked and struggled so formulate the second and third laws of thermodynamics in addition to the first. Last time we reach the third law which is telling us that we can't quite get to zero degrees Kelvin, but that as the temperature approaches zero degrees Kelvin, the absolute entropy of a pure substance in perfect crystalline form is zero. And what that corresponds to, if you recall, is the idea that in a perfect crystal at zero degrees Kelvin then you have no disorder at all. You have a perfectly ordered system. And in that case, the entropy is absolutely zero.

And the bigger lesson from that is that entropy, unlike energy  $u$  or enthalpy  $H$ , we could define an absolutely number for it. The zero of it wasn't arbitrary. Unlike the case for energy like you've seen in lots and lots of disciplines, where you can arbitrarily set the zero in a way that makes it convenient for you. Entropy really is not like that. There is an absolute zero of entropy, and that's really what we learn.

So now, now that we've got all three of the major laws of thermodynamics, what I want to start in on is a discussion of what happens spontaneously. We've seen that in just one specialized case so far, but we should in a more general way be able to tell when is a system at equilibrium, where there's no net change taking place, and when is it still undergoing spontaneous change towards some other state, presumably toward an equilibrium state. How do we tell?

So that's the topic that I'd like to address today. So, that's the big question, right? So let's say that we've got our stuff in some state. A, whatever it is. And there's some other possible state, B, whatever it is. And maybe if it some well-defined temperature and pressure. What do we do to tell whether that change will happen spontaneously? Do we calculate, you know,  $\Delta S$ ,  $\Delta u$ ,  $\Delta H$ ? What tells us whether or not the change happens? Certainly in principle we know how to calculate this and other stuff for a change in state of this sort, for lots of changes of state.

But calculating it alone doesn't necessarily tell us whether or not it will just happened of its own accord. And that's the issue that we'd like to be able to address. Now, we have addressed this in some cases. So, for example, we know that if we take, you know, gas A and gas B with a barrier between them, and we remove the barrier, they're going to mix. And we saw that and went through it somewhat carefully and saw that if the system is isolated, for that case we do have a criterion that tells us whether change happens spontaneously.

Namely, it's  $\Delta S$  is greater than zero. That tells us whether the change is spontaneous. And we saw that in fact in this case  $\Delta S$  of mixing, we calculated it, saw that it is positive. So, clearly, if we remove this barrier mixing takes place, and obviously you know that that happens from lots of experience.

In general, the second law gave us the Clausius inequality for spontaneous change. Namely  $dS$  is greater than  $dq$  over  $T$ . I suppose we could specify the surroundings temperature. We saw that in general  $dS$  is greater than or equal to  $dq$  over  $T$ . if it's a reversible process then the equality holds, but if it's irreversible, which means it happens spontaneously, then  $dS$  is greater than this. Just to illustrate the kind of issues that we're up against here, let me just consider a few different chemical reactions, all of which happen spontaneously.

So, I just want to write a few examples down with a few values for  $\Delta u$  or  $\Delta H$  or  $\Delta S$ , and see whether we can get any clues from what we see. So here are some spontaneous chemical changes. Here's one. If we take hydrogen peroxide in the liquid state, it can break down to form water and oxygen.

If we look at the thermodynamic quantities, the enthalpy and the entropy of the reaction, what we find is  $\Delta H$  is minus 209 kilojoules and  $\Delta S$  is plus 132 joules per Kelvin. So it seems like there's a favorable change in entropy going this way. That is, you've got lower energy on the right and also higher entropy. Higher entropy basically because you're forming molecules of gas where there weren't any before, and there's more disorder in the gas phase than in the liquid. That is, the gas phase molecules have more freedom to roam.

Okay, that's one example. Here's another. Let's just take hydrogen and nitrogen in the gas phase and form ammonia. Well, here we get, we find that  $\Delta H$  is negative 92 kilojoules.  $\Delta S$  is negative 198 joules per Kelvin. This one also happens spontaneously. One thing that makes it pretty clear is that certainly  $\Delta S$  or the sign of it alone is not dictating the outcome here.

All right, here's a third example. Let's take salt, solid, and dissolve it in a bunch of liquid water. Hopefully you've got experience saying that this happens, of course it does. If we measure the thermodynamics, we discover that  $\Delta H$  is 4 kilojoules, plus 4 kilojoules.  $\Delta S$  is 45 joules per Kelvin. So now we have a different sign for  $\Delta H$  and it still happens spontaneously.

So clearly, we've got signs and magnitudes of  $\Delta H$  and  $\Delta S$ , and if we wanted to put  $\Delta u$  there, similar things would happen. They're all over the map. And yet, these things are all spontaneous processes. And I didn't specify the conditions, but if we were to do this under ordinary chemical conditions of some, you'd say room temperature and pressure, right, they all happen spontaneously.

OK, clearly we'd be much better off if we had some systematic quantitative way to tell whether something would happen spontaneously. In other words, we need criteria for equilibrium under more general conditions than the

ones that we've dealt with so far, than the one set of conditions that we've dealt with so far, which is isolated system. Most chemical changes, most physical changes don't happen in isolated systems.

So let's start by writing down our definition of equilibrium. It's very simple. The equilibrium state is the one, and it's just one, in which there are no spontaneous changes that can take place to any other state. Now that's under whatever constraints there are. There's a box around it. The temperature or the pressure are fixed, what have you. But the point is, no spontaneous changes can occur to any other state. So for example, when we remove the barrier and the gases mix, you know it's over. Once the gases are mixed, there's not going to be any further net change in the system.

It's at equilibrium, under the new condition, that is with the barrier removed. OK, so now let's try to formulate how to describe the equilibrium state and what dictates spontaneity. So what we're going to do is consider the first and second laws.

So our first law,  $du$  is  $dq$  plus  $dw$ . And our second law,  $dS$  is greater than  $dq$  over the temperature of surroundings for a change that happens spontaneously. And now, I want to combine these two, which I of course can do. I can substitute  $dq$  from this expression in here. I also want to assume for our present purposes that there's only pressure volume work going on, which is to say I want to put  $p dV$  in here minus  $p dV$  for  $dw$ .

So for combining for  $p V$  work, what we see then is  $du$  has to be less than  $T$  surroundings  $dS$  minus  $p$  external  $dV$ . Or we can rewrite this as  $du$  plus external pressure  $dV$  minus  $T$  surroundings  $dS$  is less than zero. Now this is fundamentally important, and as you know that means that it warrants the exalted distinction of being put up in colored chalk. And, in fact, since we're going to reuse this again and again during today's lecture, I'm going to put it over here and leave it sacrosanct for our further use.  $du$  plus  $p$  external  $dV$  minus  $T$  surroundings  $dS$  is less than zero.

This is our condition for spontaneous change. Now this is a really quite useful expression. For one thing what we have here are all functions of state and parameters that we can control like temperature and pressure. So that's a big help. And equilibrium happens when there isn't any possible change of state that would satisfy this. In other words, you've got your system in some state.

You know it's in some state  $A$ , there are some other states around. Here is what we calculate to tell whether it happens spontaneously. So we now have a real usable criterion to help guide our understanding of whether things happen by themselves of their own accord or not. Now, this is still a little bit cumbersome, in part because of the variables involved, including  $S$ . That is, most processes that we're concerned with, they'll happen with something held constant like pressure or temperature or maybe volume.

So this isn't the most useful form that we can have, but what we'll see shortly is that from this, we can then derive further criteria for essentially any set of variables or any set of external constraints, like constant temperature or pressure or volume and so forth that we might set. And so that's what I now want to do. So I just want to use that again and again, starting from that, for various different sorts of conditions and derive the criterion for equilibrium in each set of conditions.

So first, let's start with the one that we already know, and make sure that it still works, starting from here, mainly our isolated system. So remember what that means? It means no heat, no work.  $\Delta V$  is zero.  $\Delta u$  is zero. So looking at this,  $du$  is zero.  $dV$  is zero. So all that's left is negative  $T dS$  is less than zero. In other words,  $T$  surrounding  $dS$  has to be greater than zero, and of course temperature is always positive. So  $dS$  for  $u$  and  $V$  fixed is greater than zero.

All right, so that's sounds right. That's what we saw before. When we have an isolated system, the criterion that determines whether something happens spontaneously is the entropy has to increase. Now, what this means too is if we imagine a bunch of different states, and this is the entropy of them, so this could be any sort of variable but the point is there are a bunch of possible states around, whichever one has the maximum entropy, that's the equilibrium state.

In other words, you know we've got the two gases on either side of that partition. We remove the partition, and they mix. Well, the equilibrium state is the one with the gases completely mixed. Of course there are lots of states that would have maybe local pockets of one substance in excess and another substance in excess somewhere else. In other words, there would be lots of states nearby to the equilibrium state. That is, the chain, they could they could be approached with very little change from the equilibrium state. They aren't the equilibrium state. The entropy in all of those states will be lower than the entropy of the fully mixed state.

So the point is, once you're at equilibrium none of the other states, they're accessible, the system could rearrange itself to form them, but there is no accessible state that has higher entropy than the equilibrium state. OK, that's our familiar isolated system.

Now let's try moving to unfamiliar territory and extending what we know. So, let's try constant entropy and volume. And the motivation for choosing a pair like that is easy to see, if we look at our condition for spontaneous change or general condition. Well, entropy and volume constant means  $dV$  and  $dS$  are equal to zero. What does that say? It means  $du$  is less than zero. That's our condition. So we immediately get  $du$  at constant  $S$  and  $V$  is less than zero. That's our condition for spontaneous change.

In other words, if we don't have to worry about entropy or volume equilibrium is achieved when energy is at a minimum. Now this is what you learn in elementary physics and in mechanics, right. You're not worried about

entropy. So, you know, if you've got a hill or valley and there's a cart on wheels, it's going to go down to the bottom. The spontaneous change lowers the potential energy in that case. So this is a simple condition that's very familiar. Now, the reason this condition always holds in ordinary mechanics is because you're never, in that case, concerned with a huge statistical population of particles where the disorder among them is an issue.

We're not worrying then about the fact that, well like in the case of gas molecules mixing, the macroscopic state of the whole thing, all those molecules, how many different microscopic configurations are there? Remember, I mentioned then we'll go further later on into this, that entropy can be related to the extent of disorder. That is, how many different possible configurations of all those molecules there would be for a particular state.

The reason the entropy of the mixed gases is the highest is because that has the most possible configurations. If you start segregating the gases, there are fewer possible configurations that the whole system can be in because you're forcing a particular set of circumstances. When you don't have to worry about criteria like that, ordinary, mechanical energy rules supreme, and that's dictating where equilibrium lies.

But of course, most chemical and biological systems aren't that simple precisely because you have to worry about many particles and their statistics and the way they might order or disorder. So, and of course, you know, keeping entropy as a fixed variable for a system like that is extremely cumbersome. As soon as you allow anything to mix, like you might if you want to do any chemistry, entropy changes. If you change the temperature entropy changes and so on.

So let's go on. Let's consider a few other examples. Let's hang on for a little while longer to a set of conditions where we will maintain constant entropy, namely constant entropy and pressure. So, the  $dS$  term is zero, but the other two are not. So,  $du + p dV$  is less than zero.

I can write this as  $d(u + pV)$  less than zero. Normally I couldn't do that because this term would have  $p dV$  plus  $V dp$ , but we've specified the pressure is constant, so the  $dp$  part is zero. And this is a quantity that you know, right? What's  $u + pV$ ?

STUDENT:  $dH$ .

PROFESSOR NELSON:  $dH$  less than zero, criterion for spontaneous change. In the case where  $S$  and  $p$  are held constant. Now, once again, like I illustrated for entropy, and I could have done the same for energy here, you know, if we again look at a bunch of different states, and look at their enthalpy, well, like before, they'll be invariably lots of possible states. And now, what is this saying, the equilibrium state is the one with the lowest possible enthalpy.

In the case here, that I just illustrated with the little cart going down the valley, would be exactly the same with regular energy, the equilibrium state is one of lowest energy, right. And of course there are lots of nearby states. The cart could be a little ways up the hill, and in this case, it's enthalpy, but again, there would be lots of accessible states. But if the system is in equilibrium, none of those states has lower enthalpy. It's already in the lowest enthalpy state. That is the equilibrium state.

OK, well, now, let's get to the big ones. That is, in real life, the variables that you'd normally control aren't some combination of entropy and these variables, but really their temperature, volume and pressure, any couple of those, might be what you'd really have under experimental control.

So now let's go to them. Let's control  $T$  and  $V$ . So, all right, so now we're getting serious. All right, well, there's our equilibrium criterion. We're still going back to it. It still holds. So we've now got the  $dV$  part equal to zero. So what this says is that  $du - T dS$  is less than zero, and we can combine those to say  $d(u - TS)$  is less than zero.

And again, just like before, we can do that although this normally would say this has  $T dS$  and also minus  $S dT$ .  $T$  is fixed. So that part is zero. So this is really the equivalent of this. So when we did this here, we conveniently found that that quantity  $u + pV$  is something we know and love, and we're familiar with it. It's our enthalpy  $H$ . So we could write that criterion as  $dH$  less than zero.

So here, let's combine these to define a new quantity. It obviously has importance because what it's going to say is that that's the quantity that defines equilibrium, that tells us about equilibrium, under the very important practical constraints of having fixed temperature and volume. Realistically, the more likely constraints than either of those. So let's -- we'll go to a brand new color, define  $A$  as  $u - TS$ . it's called the Helmholtz free energy.

OK, and then our criterion for equilibrium under these conditions is  $dA$ ,  $V$  and  $T$  equal to the temperature of the surroundings, is less than zero. OK, and once again, you know if we wanted to look at a bunch of states that could be accessed, well, we would find lots of states near by, in character to the equilibrium state. The one that is at equilibrium, there is only one macroscopic state at equilibrium. It has the lowest  $A$ .

In some sense, that's one reason to associate this as a kind of energy, just like mechanical energy  $u$  or enthalpy  $H$ , it's the minimum free energy state that is the equilibrium state under the relevant conditions.

Now, let's take the step to the biggest set of conditions of all. What is it when you run a chemical reaction under ordinary circumstances, what's constant?

STUDENT: [UNINTELLIGIBLE]

PROFESSOR NELSON: A little louder.

STUDENT: Pressure and temperature.

PROFESSOR NELSON: Pressure and temperature, right. You're running, you're shaking a beaker up here at room temperature. So let's look at that set of conditions. All right, there it is. This is the condition for really the lion's share of chemistry, biology, and other kinds of changes we'll be concerned with. So, there's our condition for equilibrium. We don't get to set any of them to zero, right?

So, okay and we can handle that.  $du + p dV - T dS$  is less than zero, but we do get to simplify in writing this as  $d(u + pV - TS)$  is less than zero, and just like we've seen before, yes, this has  $p dV$  and  $V dp$ , but the  $dp$  is zero because we're at constant pressure.

This has  $-T dS - S dT$ , but the  $dT$  part is zero because we're at constant temperature. So the result is we can combine all of these as a single differential, and just like we've seen before, what that suggests is that we define another new quantity given by this expression.

And that is the last one we're going to describe. And that is  $G$ ,  $u + pV - TS$ . The Gibbs free energy. Notice, we could also write, let's rewrite that.  $G$  is  $u + pV - TS$ , but  $u + pV$  is  $H$ . So we also can write this as  $H - TS$  and  $u - TS$  is what we just defined a minute ago as  $A$ . So we can also write this as  $A + pV$ . And the main thing of crucial importance is what, by defining this in the way we have, what that's saying is that  $dG$  at constant  $p$  and  $T$  is less than zero.

There's our condition for equilibrium at constant temperature and pressure. Boy, is that going to be important for the whole rest of the course. So, and of course, I hardly need to emphasize further, but we could do the exact same consideration that we have for  $H$  and  $A$ , there's  $G$ . There's our equilibrium state. It's the state that has the lowest Gibbs free energy.

All these things though are incredibly practical, useful criteria. This is only defined in terms of state functions. And just like we saw before for the case of entropy in an isolated system, now we have something we can calculate. It's a state function, so we're at constant temperature and pressure, and now we want to consider some chemical change or a phase transition or you name it. Does it happen of its own accord? Well now we know what needs to be calculated in order to determine that.

So this one is so uniquely pervasive, let's just really explicitly write it all out. For constant pressure and temperature  $\Delta G < 0$ , means  $A \rightarrow B$  is, all right, let's consider some process state  $A$  and state  $B$ . If  $\Delta G < 0$ , it happens spontaneously. If  $\Delta G = 0$ , then we're already in equilibrium.

And if  $\Delta G$  is greater than zero, then it goes spontaneously in the other direction. Any questions about any of this? Let me just give a couple of examples. If we go back to any of those chemical reactions that I wrote on the board before, right, well certainly we can calculate what  $\Delta G$  would be for each one of them. Because we know how to calculate all the parts of it. It's state functions, it's composed of state functions that we know how to calculate. So we could tell.

When  $\Delta G$  is zero, you know, it doesn't mean that you've got all of one side, all reactants and zero products or all products and zero reactants. There is some mixture of them. What this will tell us is what mixture. You know the stuff is in there in equilibrium, you know the hydrogen and nitrogen that will form ammonia. And in the end, when it's at equilibrium, and you look and you'd make a measurement, right, you could do spectroscopy.

You could easily see how much of each thing is there. It doesn't go all the way to absolutely 100 percent ammonia, zero hydrogen zero nitrogen if they were mixed together with the right ratios. Doesn't happen. There would be some of the reactants and some of the products. In the biochemical reactions that are taking place in your body, there is equilibrium between a whole myriad of reactants and products, and thank heavens that gets maintained.

So that's what this will guide us through, and of course that's incredibly, incredibly important. Here's another thing that's worth thinking about. There's a balance here between ordinary energy or enthalpy and entropy. Energy means, you know, chemical reactions happen, and you end up with something that might be exothermic, that is, the products are more stable than the reactants.

You burn methane, and it combines with oxygen to form water, to form  $\text{CO}_2$ . And if you work out the energetics as we've gone with thermochemistry, you discover there's a huge negative  $\Delta H$ . In other words, the bonds are much stronger.  $\text{CO}_2$  is really a stable molecule. Methane, there are certainly some solid bonds there, but breaking those to form  $\text{CO}_2$  and water, well it's worth it, right, energetically.

Still, the actual equilibrium depends on entropy also, not only on the energy. And that's why, when I put up those three different reactions, and we saw the signs could vary. It's because there's a balance between the two. Energy may be favoring reaction in one direction, toward let's say products that have lower energy. But at the same time, entropy is going to be favoring whichever side has higher entropy, has more disorder, and there's a balance that's achieved.

And that's why all those reactions, first of all, in some sense what I put up was kind of a trivial statement in actual fact saying they all happen spontaneously, because I didn't specify what we were starting with exactly, what concentrations we were starting with. Even something quite unfavorable might happen at least a little bit spontaneously. You'll have equilibrium. In those cases, though, you'd have quite a reasonable equilibrium,



spontaneously, that is there would be a lot of reaction that went if you simply started under practical conditions and let it go.

Even though the signs of the enthalpy changed, and the signs of the entropy changed because it's a combination of the two that matters. Here's a really simple example. Mixing of oil and water. You know from experience if you've ever mixed them to make salad dressing, they don't mix too well. And you may know that if you heat them up, they mix much better. Why?

You know, we've done a bunch of thermochemistry, and we've kind of seen that the energy of mixing, your energetics don't change too much as a function of temperature. What's changing? Why does it mix better when you warm it up? But, you know, looking at our definition of Gibbs free energy, here it is, right, or here. Let me just say, actually if you calculated  $\Delta S$  for the mixing as a function of temperature, it doesn't change all that much. You know, the amount of disorder upon mixing is not really sensitive to temperature. What does change though?  $T$ , and the entropy is weighted by the temperature, so the entropy matters more and more the hotter it gets.

And that's consistent with other things that we've seen, right? Remember the whole thing about the perfect crystal at zero degrees Kelvin has zero entropy. It's completely ordered. Entropy doesn't matter anymore. It'll go to the lowest energy state. Raise the temperature, and now entropy plays a bigger role. So the point is, this balance between energy that you could think of as say bond energies in chemical reactions, and entropy that you can think of in terms of disorder, how many different possible combinations or configurations of something wrong, will dictate where the equilibrium lies.

And knowing now how to calculate these free energies especially the Helmholtz and the Gibbs free energies, that's what's going to guide us in really calculating quantitatively, OK, where will equilibrium lie.

And before long, we'll start in on discussing chemical equilibrium, does deriving where they lie phase equilibrium? Does stuff change phase to go from liquid to solid and so forth, right? And where does that happen, at what temperature and pressure and so forth. And it's always going to come down to calculating the appropriate free energy, and how it changes in the process. So this is going to be a guide for us for essentially all that we're going to do in the rest of the term.