

[SQUEAKING]

[RUSTLING]

[CLICKING]

**GIAN PAOLO
BERETTA:**

OK, so good morning. We're back to 2.43. So let me just very briefly review what we've done the last time. We are in part 1. And we bring you some of the basic definitions up to the statement of the second law, and we have to pick it up from there. Just a quick reminder. We said what we mean by the word system. And we explained that the word system is loaded with meaning. It's not just that anything can be a system. It has to qualify.

In particular, there is a constraint on how the external forces should be mounted in your model. They must not depend on coordinates of external constituents of your system.

Later on, we'll see that there is also another constraint relating to correlations. Also, this means that your system should not depend on, or be correlated with, some other system. If it is, you have to consider also the other system in order for it to be called a system in our little business, in our little theory.

Then we define a property as being a physical observable, so something that you would obtain by probing your system in some way according to some recipe, some measurement procedure. And measurement procedures are what define these properties. And we gave the measurement procedure for energy, for example. We talked about what we mean by the word, state. It's the list of numbers that give the values of the properties at one instant of time.

And the time evolution is described by the equation of motion in a detailed model. But it can also be described by just an initial state, a final state, and a description of the effects that occurred outside of your system during that time interval. In either way, we have a few things to check.

In particular, the important business of thermodynamics is that it has to-- you have to check two things. One, the consistency with the first law, which wouldn't be a theorem in the framework in which you start from the equation of motion. Theorem of the equation of motion. And you also have to check the second law, which would be another theorem of the dynamical equation.

The idea of process, already said, is three things, initial state, final state, and effects on the environment of the system. And how do we account for effects in the environment? Well, the most we can say is how its state changes. Then by defining a weight process, namely one in which the only external effect is the highering-- lifting or lowering of a weight in a gravity field, which is a prototype of the mechanical effects, we could introduce the statement of the first law.

It is an ingredient of that statement. It says that you take any system and any-- pick any two states of that system. They can always be interconnected by means of a weight process. You-- not always you can do it in the direction you want, but if you cannot do it in one direction, you can do it in the other. And that gives grounds for the definition -- support for the measurement procedure that we introduce to define the property energy.

Without the first law, you couldn't assert that by making this procedure, you get a property, a value of a property. So essentially, this is the main-- the most important consequence of the first law is the existence of property energy, which yes, then, it is additive, it can be exchanged between systems, and it's conserved.

And that gives rise to the energy balance equation with this symbol, which you have applied in your undergraduate courses or previous-- We know every time we perform a model, we perform an energy balance to account for to check that the difference between the final and initial value of property energy is equal to the energy that-- the net energy that is being received by the system during that time interval.

So that's a statement of conservation of energy. So some people call this, "I write the first law," but I prefer to say "I write the energy balance." Then we headed towards the second law by introducing this idea of classification of states based on how they change in time and why they change in time, particularly focused on equilibrium for the moment. But later on, we will focus on nonequilibrium. And there is equilibrium and equilibrium. And we defined what we mean by stable equilibrium and metastable equilibrium.

The stable equilibrium state is most important because it enters the statement of the second law. And it is defined as a state-- an equilibrium state. So that means it doesn't move, it doesn't change in time, it doesn't move in state space. So it doesn't change with time. And you cannot change it without paying a cost, without adding some net external effects.

You need to spend something in order to change a stable equilibrium state. You cannot do it for free, so to speak. And here is the statement of the second law. It is also made up of two assertions. Let's start first with the-- we'll focus first on assertion 1.

It responds to the question, how many stable equilibrium states does a system have, in a way that is apparently contradicting what we know from mechanics, because it says that if you fix for your system the amounts of constituents, so that means the number of particles of each kind, and the values of the parameters, that is all the volume of the system, or the other things that describe the external forces, or the things that you can control from the external.

So you fix these. Then for each value of the energy, there is one, and only one, stable equilibrium state. That is the statement introduced by, I think, by George Hatsopoulos when he was collaborating with Joe Keenan in the '60s in this department. We'll talk about this, the second assertion, in a moment.

And we will see also, as we go on, that in fact, there is no contradiction as long as we understand, and we convince ourselves, that thermodynamics considers a set of states that is broader than the set of states considered in mechanics. So within the set of mechanics, there is only one stable equilibrium state, which is the lowest energy state for the given values of n and β . But in the more broader set considered by thermodynamics, there is one equilibrium state, stable equilibrium state, for every value of the energy.

And this has consequences, important consequences, that we will discuss today. Yeah, so one would ask, well, why-- I mean, we already have statements of the second law. Why do you accept this other one? Well, that's because it is more general. And it implies as consequences, as theorems,

the most famous statements of the second law, which are the Kelvin-Planck statement, called also impossibility of a perpetual motion machine of the second kind, this is the only thing we will prove today in some fashion because it's easy, is a direct consequence of the first assertion of the second law.

Later on, not today, probably next time, we prove the other statement of the second law, which is Clausius statement, the one that says that heat does not go from cold to hot spontaneously, but vice versa. That requires that we introduce-- we define what we mean by heat, what we mean by temperature. It takes a while, not long, but another lecture.

But the beauty of this construction is that you get to that result as a theorem on-- of the combined first and second law. There is also another important statement by Carathéodory, which is more mathematical, though, which can also be proved. But we will not do it in this course.

OK, so what is the perpetual-- so now, I want to talk about the Kelvin-Planck statement. What is a perpetual motion machine of the second kind? Alright, it is any device, essentially, a system in our language, that would start from a stable equilibrium state.

Remember, the state that cannot be changed without leaving some net external effects, and ends in another state, a different state, while-- in a weight process in which the weight goes up, so in which you have transferred some energy out of your system and into lifting the weight.

If you managed to do that, it's a perpetual motion machine of the second kind. It's funny because it has been very long since I have not received any emails from these crazy inventors. But perhaps because I mentioned it, or maybe Google listens, or maybe that's because I'm at MIT, but on Wednesday, I received one. I would be happy to show it to you. Very funny, somebody who wants to put a container in the sea and-- it's-- yeah, it's not even a perpetual machine of the second kind. It's of the first kind, I would say.

And I think the guy needs to learn some fluid mechanics, but in the old days, it was a continuous flow of applications for patents in-- violating the impossibility of the same. Until in the '60s or the '70s, I forget, the Patent Office, US Patent Office, decided that anything that violates the second law, or the principle, of this principle or impossibility of a PMM2 is rejected immediately without going to a referee.

That's because, as I may have told you, I forget the last time, but I remember when I was a student with Professor Gyftopoulos, he would be so well educated to reply in return and in full length to any letter that he would receive, which is a principle that I still have. But he would send, like, 20 pages to explain line by line why you were wrong and why-- and often, these crazy inventors make very complicated and convoluted reasoning that makes it very hard to dismantle and reject.

But he was doing that consistently whether you-- whether it was asked by the Patent Office or by the inventor directly. Fortunately, we don't have that sort of spam any longer. So how do we prove this? Well, one way, one simple way is to prove it if my system can be divided into two parts. So let's reason this so that we see, also, what kind of proofs, logical proofs, we are talking about.

And it is a proof *ab absurdum*. So that means we assume that the PMM2 is possible and show that it leads to a contradiction. So let us show that our system, which can be divided in two parts, that also is an additional assumption can be removed, but it makes things more complicated. Let's assume that it does start from a stable equilibrium state and it does end in a different state, A1, with as external effect the lifting of a weight.

All right. If that's true, if that happened, then you can take the energy of the weight back and use it to take one part of the system and accelerate it to some velocity. So give it in form of kinetic energy. Take the potential energy of the weight and give it back as kinetic energy of the second part of the system.

So what have we achieved? So look at this state and the initial state. Why is this not possible? Because the final state is different from the initial one, and the initial one was a stable equilibrium state. And there are no external effects because the weight went up, but then it also went down. So the net external effect is 0. Yet, we managed to start from a stable equilibrium state and change it to an entirely-- to a different state. That contradicts the definition of stable equilibrium.

OK, all right. So this is the proof of Kelvin-Planck's statement of the second law. Now, in order to go on the second aspect of this second law, the second assertion, we left behind one of the definitions that are peculiar to thermodynamics. And it's that of reversible process. What do we mean by reversible process? OK, the definition is as follows.

You have a process, first of all. So it means you have an initial and final state. And you have an external effect, B1 goes to B2. The state of the environment changes so much. OK, the process is, we call it reversible if it is possible, not necessarily retracing backwards exactly the same forward path of your initial process.

But in any other way, if you find a way to bring the state of your system back to its initial, and also the state of the environment back to its initial state, then and only then, we call the process reversible. OK, so that means you have to try hard all possibilities. So this is a very abstract definition, but it's also very precise. So I usually am not going to do it because they-- I want to make dust, but I usually take a piece of chalk and throw it to the wall, it breaks, and ask you, is that process-- was that process reversible or not?

What would you say? It is not. Fine. But how did you decide? I know it's intuitive.

Good. OK, so you use your physical intuition. That's because you have a background. You have already seen the idea of reversibility and irreversibility. But in our game, if you accept the rules of our game, what should you have done to decide? You should have tried to reconstruct the state from the piece of chalk to see if it is possible to place it back. And then also, whatever it did to the environment must be undone.

And you have to try all possible ways. So how could you be so quick in answering? OK, so correct answer, but you didn't apply our rules. This is to just underline, this is a very abstract concept, and impossible in practice. It doesn't correspond to a procedure so that you can verify if a process is irreversible or not. But it's a concept. And soon, we will find a method, and of course, as soon as we have defined entropy, that will be the method to compute, to calculate entropy, measure entropy, and see how it changes.

And from that, from the entropy balance equation, we can decide whether a process is reversible or not. So we develop a practical method to measure this very abstract concept. So why is reversible-- the concept of reversible process important in the second law? Because the second statement, second assertion, it says, you start from any state of your system and you can always go to a stable equilibrium state to bring your system from that state to a stable equilibrium state in a weight process which is reversible.

So it's all our concepts together. That's why we find them before. Now, we put them all together there. But if you go slowly and you mumble about it, that's what it says. We defined all the terms. Start from an initial state. You can always get your system to a stable equilibrium state by means of a weight process-- a reversible weight process.

It turns out that if you try other ways to change your state to a stable equilibrium state, other ways that are not reversible, you would lift the weight less than when it is reversible. So that means this is a theorem. And yeah, it's proved in the usual book. And the theorem says that the maximum lift that you can give to a weight in a weight process, with your system starting in any state, is obtained when your system ends in a stable equilibrium state and when the process is reversible.

And that final stable equilibrium state is uniquely fixed by your initial state. Only one stable equilibrium state that can be reached in a reversible weight process from state A_1 . So this is enough to say that the amount of energy that you transferred to the weight in these conditions is a property. Depends only on state A_1 . So it depends only on the time t_1 , because the final state is a function of A_1 . So it also depends on t_1 , on the state at t_1 .

And we call this property adiabatic availability of the system in state A_1 . It's the maximal-- I don't want to call it, but we could also call it work because, I mean, eventually that's a work interaction. So it's a maximum work you can extract from your system in the given state. And if you are an engineer and you're trying to make, devices to exploit natural resources like energy resources like coal, natural gas, nuclear, whatever, solar, you--

The main question that thermodynamics was set for 200 years ago by Carnot is, well, what's the most I can do out of this situation? And adiabatic availability is an answer. Of course, it gives an answer under certain conditions. You change the conditions, you get different answers. As we will see, we will have more availabilities. It depends on the condition. Here, the condition is in a weight process. So if I have my system, and I confine myself to just a weight process, that's the amount, the maximum amount of energy I can extract from my system.

The most I can do out of it. If it weren't for an important detail, we would be satisfied that the adiabatic availability is all that we need in order to describe our engineering applications. The detail is that this property is not additive. And therefore, it's not very practical because when you have a system made out of two subsystems, and you measure the availability, the adiabatic availability of system A and then the adiabatic availability of system B, well, if you want to consider the combined system, you have to make another measurement to measure the adiabatic availability of the system C.

The simplest example that I can think of is, suppose you have a glass of water, which is hot and a glass of water which is cold. So you measure the adiabatic availability of this one. And if it is hot, but in a stable equilibrium state, how much is the adiabatic availability? It's 0 because otherwise, it would be a PMM2. I mean, if you could-- if you started from a stable equilibrium state, you cannot lift a weight.

So a system in a stable equilibrium state has 0 adiabatic availability. So the adiabatic availability of, we use a letter ψ , so of this glass of water is 0. Also of that glass of water is 0. But if I consider the composite system, of course, we all know that, for example, with the Carnot engine, you can extract work out of this situation. So you see that 0 plus 0 does not make a number of different from 0. So we lack additivity of this property.

And this is why it takes the next half hour to build up another property. It will be entropy, which will contain features so that we can compute the adiabatic availability and it will be additive. We have to build additivity on-- around adiabatic availability. There is also this other theorem that I'm not proving. But I'm pointing you at this proof. It's on page 76 of the book.

Again, so since I'm not doing it, I'm not asking that you study it. But if you're curious and just go and look. It says that if you consider a weight process, so now, we confine ourselves to a weight process, between any two states, so clearly, if you-- since adiabatic availability is a property, you can measure it for state A1. You could also measure it for state A2. Like, energy, the property, so you can measure it for A1 and you can measure it for A2.

So you give me two states of system A. And I can measure for each state its energy and its adiabatic availability. So it turns out that this theorem says if you have a necessary and sufficient condition for the process to be reversible, if the difference between energy and adiabatic availability, so you could interpret that as the energy that is not adiabatically available at the end, is equal to the energy not adiabatically available at the beginning.

So in a reversible process, the energy not adiabatically available is conserved. Whereas in an irreversible process, it increases. Very similar, in fact, also entropy will play the same-- will play in a similar way. So this energy that is not adiabatically available is a witness of reversibility. It's the basis for measuring in practice whether a process is reversible or not.

All you need to do, according to-- if you trust this theorem, is measure energy and measure adiabatic availability with the tools we developed and then check this inequality. If it is an equality, the process is reversible, the reverse-- sorry, the weight process is reversible. If it is an inequality like this one, the process is irreversible.

If it's the other way around, it's impossible. You made be something wrong. It is impossible to decrease the amount of energy that is not adiabatically available. So this is a precursor of the principle that we will call of entropy non decrease-- we could call it the principle of non decrease of the energy, nonadiabatic-- adiabatically non available.

OK, so now, we try to make or build up this property. There has-- that builds additivity into adiabatic availability. So we are heading towards entropy. In order to do that, we introduce some other concepts.

The first one is the concept of mutual stable equilibrium, or mutual equilibrium, between two systems. So two systems are in mutual equilibrium, like the hot and cold. These are not in mutual equilibrium because the composite system is not in a stable equilibrium state. The fact that it has adiabatic availability, because that's an if-and-only-if theorem, so the fact that it has non-zero adiabatic availability is equivalent to not being a stable equilibrium state.

So these two, they are individually in stable equilibrium. But the composite is not in a stable equilibrium state. So they are not in mutual stable equilibrium. In another situation in which instead, they are individually, and also the composite system has zero adiabatic availability, so that means the composite is in stable equilibrium, then you say that the two systems are in mutual equilibrium. That's the concept.

The other concept is that of thermal reservoir. A thermal reservoir is a particular system, I would say, a limiting system, that has this feature that I will describe with a practical system that we can make in any lab. You take a substance, like water, in a fixed volume container and you produce a combination that we call triple point. So a situation in which you have the coexistence in stable equilibrium of ice, liquid water, and water vapor. Right here, ice, liquid water, and water vapor.

OK, then you find another system, let's call it C, that is in mutual equilibrium with it. For example, it could be another copy of another piece of water at the triple point, but not necessarily. The important thing that defines a reservoir, a thermal reservoir, is that if you change the energy of this particular system, for example, I consider a state with more energy. So it will have lesser ice and maybe a little more water vapor or less liquid water.

In any case, so the proportions of the three phases changed. So these are two different states with different energies. But they are both in mutual equilibrium with the system C. Now, why did I choose triple-point water? That's because it is easy to prepare in any lab. And as you know, we haven't defined what the temperature is. In a moment, we'll do it. But just because you know what temperature is, a triple point is at a low pressure like 0.6 kilopascal and at a temperature of 273.16.

So it's 0.01 Celsius. OK, now that we have the reservoir, we apply again the second assertion of the second law, which says we can always start from a system in any state, and reach a stable equilibrium state in a reversible weight process.

This is an important loaded statement. It allows-- I mean, how do I know that it always exists? It's very abstract. But it's very similar to the statement that says in the first law, the second assertion, that says yeah, you can always interconnect the two-weight processes-- I mean two states by means of a weight process.

But no matter what weight process you choose, it's always the same energy that you transfer out to the weight. So how do you know that by-- because I can invent many different ways to do that job. And how do I know that they will all get the same outcome? OK, that also is a very abstract idea. But it works because energy has-- after all, has been very successful in describing stuff in physics. And we believe in it so much to be one of those great conservation principles that we talked about last time.

And here is the same thing. We have a very abstract idea about the existence of something. It guarantees that now, we define a measurement procedure based on this one. If we didn't have this statement, we couldn't trust our measurement procedure. And the measurement procedure is based on this ingredient, which I repeat here, with a little more detail. So I take the system and the reservoir. And they are in some initial states, A1 and R1.

The reservoir starts in a stable equilibrium state, like water at the triple point. Then I do a reversible weight process for this combination, for this combined system, composite system, which has as only external effect the lifting of a weight. And it's maximal lifting because the process is reversible-- because the weight process is reversible. So that's the maximum. We are applying essentially the theorem of adiabatic availability here. But to the composite system, A and R.

All right. If this listing is maximal, then-- and I think I jumped a little bit. But maybe I could say that if the final state-- in order to apply the theorem of adiabatic availability, the final state would have to be a stable equilibrium state for the composite system now. And by our definition of mutual equilibrium, it would mean that since the composite is in stable equilibrium, the two parts are in mutual equilibrium. It means that the final state A2, the system A is in mutual equilibrium with the reservoir.

Here, I want to do it a little more general. And you see I'm applying that theorem twice because I'm going-- in order to go from A1 to A2, I could-- in which my reservoir is in R1 and here is an R2. So now, I do consider the composite of the two systems.

The theorem of adiabatic availability says that if I go, let's say our-- let's call it RR. OK, so if I go from here to here, and this one is a stable equilibrium state for the composite, then I have extracted as much as I could.

Also, I can do it starting from state two. So here, I would extract the adiabatic availability, let's call it ψ_1 of the composite system, AR. And here, I would have extracted the adiabatic availability of the system in this other state, 22. OK, but since in doing this extraction, I'm using reversible weight processes, I can also reverse the arrow. So I can go this way. And of course, I undo the effect on the weight.

So as I go from here-- so that means I can go from here to there by means of that reversible weight process. And the amount of energy I transferred to the weight is a ψ_1 minus ψ_2 . OK, however, in this-- the ingredient-- yes, so we know how much energy we transfer to the weight in that process on the slide.

But for the measurement procedures that we are going to introduce in a moment, what's important is the change in energy of the reservoir. How much the energy of the reservoir changed during this process, because that's something that we can measure.

You do that process, so you give me a system A, you choose two states A1 and A2. The second law guarantees that you can do this process with any reservoir. And then once you've done it, you can measure energy because we defined property energy. And so measure it for the reservoir and make the difference of the final energy of the reservoir and its initial energy. Now, this symbol here is complicated because I want to emphasize that, yes, we are measuring an energy difference for the reservoir, but it's more than that.

We have to do it in those particular conditions. So it says that system A starts like this and so on, that the process is a weight process and that it is rigorous. You do it under other conditions, it's another story. OK, all right. So this is the ingredient. OK, with that ingredient, here is the measurement procedure that defines a property that we will call temperature of the reservoir. And that will turn out to be a constant for a given reservoir.

So equal for all of its stable equilibrium states. We already know for-- we already know that for the triple-point water, it's 273.16K or 0.01 Celsius. And in fact it is-- for as long as you-- in the box, you have all three phases, you can put in energy, take energy out, and so on. As long as you have at least some ice, some water, and some water vapor, that temperature doesn't change. So it's equal for all the states of that system.

OK, but how do we measure it? OK, so now for this measurement procedure, the object of measurement is the reservoir. You come to my lab with your reservoir, and I am supposed to measure this property for your reservoir. So here's the object. In order to do the measurement, I take an auxiliary system. So I choose whatever system I want and any arbitrary two states for that system. And I do my reversible weight process for the combination that will lift the weight by somehow, some amount.

And I measure how much your reservoir changes in energy. And I put that in the numerator. In the denominator, I put the result of the similar measurement that I have done once and for all for a reference reservoir, which I happen to like to choose the triple-point water. Of course, when I need these measurements, I use the same system A and the same two states A1 and A2. OK, and I measure how much energy changes this reference reservoir. And I take this ratio.

So this ratio is a measurement by comparison. It's exactly like when you say, well, how long is this thing? OK, you compare it with the meter or the inch. And the meter is another object that is maybe in some museum in Paris. But and you see how many times this thing stays. So take the ratio of this length to the length of the meter. You get a dimensionless number. It's exactly like here. It's a dimensionless number.

As you know, when you have measurements like that, you can introduce a unit of measure. You call the meter 1 meter, but you could have called it, I don't know, how many inches are in a meter, but you could call it like 40 something inches. OK, in this case, we take the ratio, we multiply-- we take as a unit, not 1 Gibbs or 1 Hatsopoulos, but we call it-- since Kelvin was the first. We call it-- and he didn't put 1, but he put 273.16. Alright. So that's our basis.

But we put here this number in the result. So you multiply by that number, this dimensionless ratio, and you get this property temperature in kelvin.

Of course, there is an important theorem. Again, it's proved there, that says, first of all, that this ratio is positive, that it is independent of the initial states of the reservoirs, that it is independent of your choice of auxiliary system. And once you've chosen that system, independent of the initial and final states A1 and A2 of that system. And also that it is equal for all stable equilibrium states of a reservoir.

So that is a property having a constant value. We call it a temperature of the reservoir. Notice, we define just the temperature of the reservoir. We haven't defined yet the temperature of a stable equilibrium state of a general system, not yet. But this is enough for our purposes.

Also, notice that, by the way we define the property, so this formula, you can rewrite that formula by taking the things with the subscript R on the left-hand side and subscript R0 on the right-hand side. You get this other equality. From this equality, you can infer what, that if I measure this ratio for reservoir R, it's the same as for the reference reservoir. It's the same for all reservoirs. So it's independent of the reservoir.

So this ratio, although we use the reservoir to measure it, is independent of the reservoir. So what does it depend on? It depends only on the system A and the auxiliary system that you have used, and the two states. This is why this is very important, because essentially, this leads us to the definition of entropy. That ratio, we call it the entropy difference between two states A1 and A2 of our system A.

If you want to put it in another way, what's the measurement procedure for entropy? OK, so now, you come to my lab and bring your system and bring the system in a given state on which you are interested in measuring the entropy. Again, I tell you, look, I just can measure entropy differences. So I will pick a reference state A0, give it whatever value you want for the entropy of that one. I'll measure only the difference. And how do I measure the difference?

Well, I run-- I find a reversible weight process for your system and my reservoir. For example, I could choose water at the triple point, but not necessarily, and measure the energy change of the reservoir using this process and put it at the numerator. In the denominator, I put the temperature of the reservoir that I have previously measured with that other measurement procedure. And this ratio we just proved is independent of the reservoir I had chosen here.

So I add this ratio to-- so this ratio essentially is the answer. That's the difference in entropy between these two states. All right. So we have an explicit measurement procedure that gives us entropy. And the advantage of this property with respect to adiabatic availability is that it is additive. You do it for a system A, you do it for a system B, and then you do it for a system composite AB, well the entropy is the sum. The entropy differences are additive.

In a moment, we will see also, a practical engineering meaning of entropy. But let me also define this other property, which we essentially already did here.

When you have a system in combination with a reservoir, like here, a system and a reservoir, they start in some initial states the reservoir in a stable equilibrium state system A in any state, equilibrium or non-equilibrium doesn't matter. I can apply the theorem of adiabatic availability to the composite system and find that the maximum weight lift that I can obtain from this composite system in those initial states,

is the adiabatic availability, is obtained when we make the weight process reversible. And it also ends in a stable equilibrium for the composite system. So when the two-- when A and R are in mutual equilibrium. So here, system A ends in a state that I call $A_{sub R}$ just to remind us that it is the state in which system A is in mutual equilibrium with the reservoir. And the final state of the reservoir is also uniquely fixed by the initial states of A and R.

OK, this is a new property. You can view it-- if you fix the reservoir or with respect to a given reservoir, this is another property for system A. It is another availability, another maximum work in other conditions when the system can also interact, or has a reservoir available with which to interact. We call it available energy with respect to the reservoir R.

We can make-- so we call ω . ω is the energy that goes through the weight. We can make-- you can write an energy balance for that process because now, we know how to compute the energy. So we can compute the energy difference for system A. It goes from A_1 to A_R . So the energy that goes out of system A is E_1 minus E_R . The energy that goes out of the reservoir is E_{--} the energy of R at state S_1 minus the energy of R in this final state.

And since the energy is conserved, these are the things that go out. They sum up to what is received by the weight. So this is the energy balance. But now, if you remember how we defined the entropy of system A, just previous slide, it's the ratio of the energy change of the reservoir. So it's this much. The change is actually final minus initial. So it's minus this much, divided by the temperature. So that's the entropy. So this ratio-- we could substitute this part using this equation and make an expression for the available energy in terms of the entropy.

I hope you see the algebra here. So this is the working equation for computing available energy of a given system. All you need to know, available energy with respect to the reservoir R, you need to know the initial energy and the initial entropy E_1 and S_1 . You need to know the energy and the entropy that the system has once it gets into mutual equilibrium with the reservoir. And you need to know the temperature of that reservoir. And this is a combination.

If you-- we call it available energy with respect to the thermal reservoir R. Later on, when we say a few words about exergy, and this is one form of exergy. Exergy is a word that was invented during the '70s or maybe earlier. Keenan and called it availability in 1941. So this concept is around for-- has been around for a while. But exergy, the ex means it's like the essential part of energy because essentially, exergy is the answer to the question, what's the maximum I can do for-- from a given situation? So there are many exergies.

And we already have seen a couple. Adiabatic availability is an exergy that applies when the system undergoes just a weight process. Here, we have available energy. It's another exergy that applies when a system also has available a reservoir. It is the combination of the system and the reservoir, which undergo a weight process.

So this is the formula. So let's play a game here. Let's play a bit with the formula and rewrite it in this way, putting in evidence the entropy of state one of a system. Yeah, before I do that, notice that except for the temperature of the reservoir, this formula doesn't have any other properties of the reservoir. So it doesn't have the difference in energy as has disappeared because we wrote that in terms of the entropy change for the system.

OK, so we put in evidence of the entropy of system A state A_1 . And we notice that except for some things that are constant fixed by the chosen reservoir, the entropy is proportional to the difference between energy and available energy. So again, it is the energy that is not available with respect to the reservoir divided by the temperature of the reservoir.

So the entropy is proportional to the non-available energy with respect to the reservoir. So the higher the entropy, the lesser the energy that can be transformed into lifting a weight, which is the prototype of a useful effect, mechanical effect. So that's why I call it engineering meaning of entropy. A lot of mechanical engineering, energy engineering, is related to trying to exploit as much as possible the availability of systems, and in other words, to-- and entropy plays against it.

You let entropy increased, you lose ability to do useful effects. So that's why in engineering, we have to work in trying to improve the efficiency of stuff, of machinery, and so on. With the purpose of reducing the spontaneous generation of entropy because that will kill the available energy.

OK, we said-- already said that the entropy is additive, that it can be proved that it is additive. And then, the theorem on the criteria for reversibility. We have already seen the first line here expressed in terms of adiabatic availability of the system. You can express the same. That theorem translates also for available energy. So the difference between energy and available energy in respect to any reservoir, any given reservoir, remains constant in a reversible process.

So the unavailable energy remains constant in a reversible process while it increases in an irreversible process. And it cannot decrease. And since we just saw that this unavailable energy is proportional to the entropy, we can write this as S remains constant in a reversible weight process. Energy, I'm sorry, entropy increases if the process is irreversible. Entropy cannot decrease in a weight process.

Careful here about the conditions that we made this statement in because it would be wrong to say, ah, energy-- I mean, the entropy cannot decrease. The entropy decreases all the times. Whenever you take a can of Coke and put it in your refrigerator, the entropy of that can of Coke decreases because you're cooling it down. That is not a weight process.

What we're saying here that the entropy cannot decrease in a weight process. If the only external effect is only the changing-- I mean, the lifting or lowering of a weight, then you cannot decrease the entropy. But you can decrease the entropy of a system by simply taking making it flow out of your system because entropy is actually transferable.

We prove that in the same way as we did for the transferability or exchangeability of energy. We consider a composite system, you apply-- if I do it for a reversible process, then entropy remains constant. So it's a principle of entropy conservation in a weight-- a reversible weight process.

You combine it with additivity, you find that the entropy cannot disappear. If it goes out of system A, it means that you find it somewhere else in system B, in a reversible weight process. So in the same way as we decided to give a symbol to this amount of entropy that is transferred from one system to the other, we use a symbol that is similar. So S for entropy transferred from B to A in the direction of R arrow. So it's a positive number if the flow is in the direction of the arrow. Otherwise, it's a negative.

And so we can write this as a balance equation, a balance equation. For a reversible process, you wouldn't have this power. But simply say if there is a change in entropy of your system, it is due to the amount that it has-- of entropy that has been transferred with this environment. But then entropy is not really always conserved. It's conserved only in a reversible process. In an irreversible process, it's not conserved. And if the process is a weight process, it can only increase.

So that means that the entropy change of my system can be greater than the amount it received but cannot be lower. So essentially, we are writing an imbalanced equation, a balance equation if you want. It becomes a balanced equation if you put in the balance also the imbalance by calling it entropy generated, or produced by irreversibility. And this brings us to the entropy balance equation.

I assume that you have played with this in solving problems in undergraduate thermodynamics and in your applications in energy or exergy analysis, any technological problem having to do with energy transformation of energy in various forms requires you to make not only an energy balance, but also an entropy balance.

And the combination of the two is what allows you to determine things like how good am I doing? What's the efficiency of what I'm doing? So these balance equations, as we'll see more explicitly, are the fundamentals to define efficiencies of power plants and any device that does transformation of energy.

OK, this is also the version of the entropy balance, the rate version of the entropy balance. If you have the kind of description in which you can follow as a function of time, the state of the system, and therefore, you can measure as a function of time, the entropy, and also how much entropy is being exchanged, so the rate of entropy exchange. And remember that in an entropy balance, there are three very distinct elements. There are three parts of that equation.

The left-hand side says how much the property changes from the final to the initial state. The transfer term says how much the system, the net entropy that has been received by your system, or exchanged, if it is negative, it's given out by a system due to interactions. It's a flow of entropy going in and out of your system.

The last term instead is the generation. It occurs internally to your system. It's the dissipation. It's the waste and the curse. If you let things move around. For example, if you take Irish coffee, no, it's very nice if you-- until it is separate. The first time you see it, you are excited. If you stir it, you lose the beauty. No? And by stirring it, you have mixed up things. You have produced-- generated entropy. You've lost, I mean, the beauty because you are sort of a bit drunk. And so that's--

But this gives the idea of the fact that stirring is something that happens spontaneously. If you help it by stirring it, it goes faster. And it's something that you cannot undo. I mean, the Irish thing will not separate. Maybe it will but not enough-- not if you are talking about energy applications. So if you're not careful enough, and things get stirred up, you lose opportunities to convert the energy and to extract energy out of your source. And you've lost it forever.

OK, luckily. I don't think this time-- I don't think today, but the next time, we will be able to introduce a graphical representation of all that we have said that is very useful to remember and to reason the various consequences and also to set up problem solving and answering additional questions. It will be the energy versus entropy diagram.

But we are still building up material so that we can use that diagram to summarize what we have seen so far. And one of these ingredients that we still need is another theorem that is called the maximal entropy principle, which says that among all the states of a given system, once you fix the values of the amounts of constituents and the parameters of the external forces.

And you consider-- of course, you remember that if I fix the amounts of constituents, let's call them n of t , let's forget the t , n , and β , this doesn't fix the state because the state is these numbers plus the values of all the conceivable properties.

Most of the times, this list is an infinite number of numbers. So fixing just these two leaves you, again, with an infinity of states. Now suppose I fix also the value of the energy. OK, so I fix this much. Still, I have a lot of states. They will differ in the values of all these other properties, but they have the same energy. OK? So if I consider all these states that have the same energy, amounts of constituents and parameters of the external forces, it's a set.

In this set, the second law, first assertion says there is a unique stable equilibrium state. This theorem says that state has also the highest value for the entropy. And it's a strict inequality. It's the only state that has that value. All other states with the same energy and so on have lesser entropy. The stable equilibrium state, among these ones, is the one that achieves the maximum value. And it is the only one that achieves that value. This is called the maximum entropy principle.

There is also a dual principle that is called the minimum energy principle. It's similar to this one, except that here, you put S . So if I consider all the states of a system that have the same given-- same values of n , β and the same entropy, then among all these states, there is one stable equilibrium state only. And it is the lowest energy. When you fix the value of S to 0, that corresponds to the domain of mechanics.

And that minimum energy stable equilibrium state is the only one. And so then we recover the minimal energy principle of mechanics. But thermodynamics is about states that have also entropies different from 0. And so we have a more general minimum entropy principle. Yes.

Yes. If you start from the low-- a stable equilibrium state, like this one is a stable equilibrium state. If you spend some work, so if I go this direction and I spend some work, I can obtain any other state, any other state, but only those that have the same entropy as I started with. If the process is reversible, I-- the entropy will remain constant. So I can go from my minimum energy stable equilibrium state to any other state which has higher energy because I put in some work.

But if it is reversible, it has the same entropy. If it is irreversible, it will have higher entropy. So it can go only, let's say, from here with energy, I can go up. And this is entropy. So this will-- OK. So I start with a certain value of the entropy, say S_R . I can go up in a reversible process to values of the energy higher than I started with. So this is E_R . Or I can also go to the right because I put in energy but if the process is irreversible, I generate some entropy.

So the entropy adds. And I go to the right. So yes. Thanks because this anticipates essentially this energy versus entropy diagram, and which is useful because as you know, a picture is worth a thousand words. And this is the picture that allows you to answer these kind of questions. The last ingredient that we need in order to go to that graphical representation is called the state principle.

Again, it is a consequence very directly from the first assertion of the second law, which says you fix n and β . Fix n and β , you fix the energy. And once these are fixed, there is a unique-- there exists a unique stable equilibrium state.

Alright, the last S means state. So yes. It's a state which is stable equilibrium. So what does it mean, state? State means the values of all the properties. So that means that this thing fixes the values of all the properties. Of course, you're talking about of a stable equilibrium-- of a stable equilibrium state. So we-- so mathematically, that's exactly what we mean by a function.

The properties, it means that these properties, any property, is a function of these numbers. If these numbers fix the value, that's what we mean by value of a function. So we can write a property of stable equilibrium, at stable equilibrium, as a function of the amounts, the parameters, and the energy.

And since among the various properties we defined one is entropy, we can also write that for the entropy. So we can say that for the stable equilibrium states, the entropy, the value of the entropy, is fixed like all other properties by the amounts of constituents, the parameters of the forces, and the energy.

This expression, this formula, this function is called the fundamental relation for the stable equilibrium states. In some old-fashioned books of thermodynamics, this function is page one. You take the book by Callen, Callen was a PhD from MIT also. Very nice contributions.

But in his times, thermodynamics was only about stable equilibrium states. And so that's the starting point. And since I'm at it why not saying and reminding you that instead, we've seen a definition of entropy today in which you may or may have not noticed, but I will stress it anyway, that we never said anything about how many particles the system should have.

In our game so far, we could have a system with one particle or 10^{23} . It could be just water in a box or a nuclear power plant, complex or simple, small or large. Plus, we didn't make any assumption about the kind of state. In fact, the most interesting states are those that are not stable equilibrium, at least from the point of view of making a weight process, because in a stable equilibrium state, we just have seen that the perpetual motion machine of the second kind is impossible. You cannot extract work. So not very useful from an engineering point of view.

And that's why-- consider the ocean. The ocean as a thermal reservoir. Not the waves, that's a different story. But as a thermal reservoir. And if you forget also the fact that inside there are temperature gradients, and also salinity gradients, and so on. But if you think of it as a huge system, so it has a huge amount of energy. But that energy is essentially useless. The thermal energy is useless because it's in a stable equilibrium state.

Whereas if I have a system in a non-equilibrium state, and I'm quick enough to extract its adiabatic availability, I can do something useful. For example, we will do later on in the second part, we will do, like, chemical reactions. You think of what happens inside your internal combustion engine. You've got the piston, you got a mixture of air and gasoline, and you light the spark. At that moment, you produced a non-equilibrium state, which very quickly in the matter of micro-- milliseconds, will interest the entire combustion chamber. Pressure will go up and so on.

The internal combustion engine is an incredible device that has been there for a century now, maybe longer. And it's still powering our cars. And because it's a smart way to extract the availability. It doesn't do the entire job, though, because it loses the opportunity that you have from when you light the spark to when the flame is engulfed the entire combustion chamber. That is a very irreversible process. And that's where you lose the-- about, what is it, 60% of your availability, no, because the internal combustion engine is 40% efficient.

So it means that I lost 60% somewhere. And that's where I lost it. So, non-equilibrium states. And so we define entropy also for non-equilibrium states, which is most important for the more modern applications of thermodynamics. And that's why we're here. Actually, I was very happy just yesterday to receive an email. I think it was sent to the entire community, not very special. But an email from the MIT president announcing this initiative about climate.

A lot of the applications that will come out of that project in the future will have to do with energy and the best use of energy. OK, not only CO₂ segregation, or greenhouse gases, but all the crazy ideas that people are talking about in trying to control, for example, the amount of heating that comes from the Sun.

There was an article the other day in the *New York Times* talking about people that want to build shields in space, no, to reflect away some of the power, some of the photons, that come from the sun so that you could control temperature.

Of course, you need a surface to, I think it was the surface of the entire Argentina, which is essentially half of South America. Somewhere put in a place, which they call it a Lagrange place, or a Lagrange spot where it would stay because the gravitational force on the sun is on the Earth is the same. All right, so yes, crazy ideas.

But one tool with which you have to evaluate these ideas and see if they are feasible or not is precisely what we are doing here for any energy technology, or for any technology, you have to see that you're transforming forms of energy, or you're spending energy to recover another effect. You have to define efficiency. Feasibility and efficiency are very important, no, because if you-- if the amount of energy you're consuming for a certain task is more than the work, minimum work to do that task, it's worthless.

You better not do it. Do it in another way. OK, so what I'm saying is that somehow, by learning these tools and ways to understand the equilibrium and the non-equilibrium for small-- and for large and small systems, you are in good position to go and contribute to this very bold MIT project, new MIT enterprise for the next 10 years.

So that brings me to, yeah, one more thing. And then just we have three minutes. Once I have a function, like this function here, then I can apply all the tools of mathematics. For example, if I am interested in looking at how the function behaves in the neighborhood of a given point, so here's the function, and here, and I want to see how it behaves in the neighborhood by changing one of the variables, for example, the energy, I can write a series expansion of the function.

I take derivatives, first, second order, if the function is regular enough so that you can take at least two-- the first two derivatives with respect to all the variables, you're in good shape. In practice, in most of the models, the function is analytic, so if there's all derivatives. Some of these partial derivatives will turn out to be useful and to be important in determining necessary conditions for mutual equilibrium between systems.

And it turns out that all the first derivatives, the first partial derivatives of this function here, play a role in determining those mutual equilibrium conditions. And that's why we give names. For example, in the derivative of S with respect to E , is the inverse of what we will call the temperature of the stable equilibrium state of the system.

Yeah, that's because I write it also this way as a derivative of S -- of E with respect to S because once you have a function, and if it is well behaved enough so that all the derivatives are not neither 0 or infinite. So you can invert the facts. OK, there are mathematical theorems for inverting functions.

So if I have this function of S as a function of E , I can also most of the times write it as E is a function of S . If I can do that, not for all systems, we'll see you can do that. But if you can't do that, then you have another version of this fundamental relation, which is the energy form, because it makes energy explicit and entropy becomes a dependent-- an independent variable. And you can also take derivatives of this one. So the partial derivative of E with respect to S is going to be what we call the temperature of the stable equilibrium state.

The partial of E with respect to n is going to be the total potential, or chemical potential, depending on situations. And if one of the parameters is the volume, the partial of the energy with respect to the volume is what we will call the pressure with the negative in front-- sign in front.

So these partial derivatives are related to conditions for mutual equilibrium, and are also therefore related to instruments with which you measure them by exploiting the mutual equilibrium condition. So you can have the thermometer, the manometer, and the, again, a manometer that allows it to measure partial pressure so that you can compute the chemical potentials.

All right. So we are out of time and we stop here. So next time, we go to the energy versus entropy diagrams to summarize all that we have seen, and go further.