[SQUEAKING] [RUSTILING] [CLICKING]

GIAN PAOLO BERETTA: Good afternoon. So here we are. And let's see where we are. We have introduced this energy versus entropy diagram to summarize concepts. And we have obtained these important inequalities that I called generically Clausius inequalities that essentially talk about-- say something about how much entropy must be exchanged between two systems if these two systems start in stable equilibrium states and they need to exchange energy with no other effects.

So if this is the curve for the stable equilibrium states for system A and this is for system B, we suppose that the system A starts in this state and that we want to extract this much energy from it and give it to system B. We realize that there is no way to-- since there are no states below the initial state, we need to extract also some entropy.

But the problem is that system B-- so if we extract entropy from system A, that entropy can only go into system B because there are no other external effects. But starting from this state, system B, and receiving this much energy, the amount of entropy that it can accommodate is only this much, which is called S max. So that's the maximum amount of entropy that B can accommodate.

Whereas for system A, this is the minimum amount of entropy that it needs to give to system B in order to find a state with this lower energy level. So we are left with a possibility of possible states that are on these dashed lines for system A and for system B that correspond to entropy transfers within the range allowed by these constraints that we have described.

So that turns out to be writeable as a couple of inequalities. The Clausius traditional statement is, as we have seen it, for infinitesimal amounts of energy transfers. This is for finite. But the concept is the same. So today, I wanted to talk about some traditional results. And we still need to define what we mean by heat. First of all, we define what we mean by work. So work is a mode of interaction in which there is no entropy transfer and no transfer of amounts of constituents.

So that's, for example, what happens in a weight process. In a weight process, if during the entire process, there are no external effects, then the weight process experiences-- the system experiences a work interaction. As you may read here, it says that the weight process may be adiabatic. We call adiabatic a process in which there are only work interactions.

And then we say, well, a weight process may be adiabatic. Why maybe and not is adiabatic? Well, because a weight process is a process in which the only net external effect is the lifting or lowering of a weight, the net effect. But you could have some temporary effects that are initially done and then undone, which may not be describable by lifting or lowering a weight.

So in that case, it's still a weight process. But during the process, there were interactions that may not be work. But for simplicity, if you want to fix ideas, a good example of an adiabatic process is a weight process in which there are no entropy transfers all along the process.

Anything that has an entropy transfer, we call it non-work. So non-work is a very broad class of processes, of types of interaction. And in this broad class, there is one limiting condition that we call heat interaction. So we will see in a moment what is the defining idea behind what we call heat. It is a limiting process. And it doesn't exhaust all the possible non-work interactions. So not all non-work interactions are heat.

And in fact, I already anticipated the last time that, during a heat interaction, we have a very well-defined ratio between the energy that is exchanged, that we call heat, and the entropy that is exchanged. And the ratio is equal-- energy over entropy is the temperature at which that interaction occurs, so much that therefore, in order to characterize a heat interaction, we only need to say it's heat, how much energy is transferred, and what is the temperature at which it is transferred.

But what's the defining criterion for heat? One way to put it is, we want to define an interaction, which is completely distinguishable from work, so an interaction in which these two systems, say system A and system B, exchange energy and entropy. And nothing, no fraction of the energy that is exchanged between the two, can be recognized as work.

What does it mean? All right, we do it operationally. Let's say that we extract some energy from system A. And let's suppose that we intercept that energy. And before giving it to B, we feed it to some machinery, some machinery that will try, at its best, to split that energy into a part that is recognizable as work and the rest.

Sometimes, I mean, traditionally you would call it a Carnot engine. But let's call it a cyclic machinery, cyclic because it has to return to its initial state. And so whatever it does, it's not because you consume the machine, but because of the operations of the machine.

OK. So in this situation, suppose we extract this much energy and this much entropy. We feed it to the engine, to the machinery. How much work can we extract? Well, this is a standard problem in thermodynamics that gets solved by writing energy and entropy balances.

So we write energy and entropy balances for system A and system B. We also assume that system A and system B begin and end in stable equilibrium states. And we write this bunch of equations. If you count the equal signs, it's how many equations? 1, 2, 3, 4, 5, 6, 7, 8 equations.

Considering the initial temperatures as fixed parameters, the variables here are the various entropy exchanged and the energy and entropy changes for system A and system B. If you count them, I think there are nine variables, eight equations. You cannot solve the system. But you can solve it for a ratio of two of those variables.

And we choose the ratio that we are interested in, namely the work that has been separated out of that stream over the inlet energy, inlet into the cyclic engine. So this ratio, as we all, because we've all taken thermodynamics before, it's the Carnot ratio between the two initial temperatures of these systems.

So this says that if these two temperatures are different, this ratio is not 0. It's a definite number. Suppose the system B is at 300K and system A is at 600K. This is 300 over 600. That Is 1/2. So 1 minus 1/2 is 50%. So that means that the cyclic engine here could split 50% of the received energy from A and make it go into the work channel.

Sure. If we want to complete the job once, we have split this energy and give it to the weight, then we take the weight back and give that energy to system B. So the end result is the same. We transfer the energy from A to B with no external effects. But in between, we manage to recognize a part of what flows from one system to the other as work. That's not what we want to call heat. We will call heat only in the limit in which this ratio goes to 0. And that goes to 0 only in the limit in which the two temperatures get equal or very close to one another.

And in terms of that train of inequalities that we have seen, the Clausius inequality last time, that interval of values, if the two temperatures are equal, shrinks to a single value. And therefore, we get a definite entropy transfer for a given energy transfer. And that's how we get the famous equation that delta S, the entropy exchanged, is the energy exchanged over T, so Q over T.

And of course, I have stressed it so many times. But we noticed that we have defining heat here using entropy. Usually, it's the other way around. The traditional expositions start from some hand-waving definition of heat, and then some definition of temperature. And then Q over T becomes the entropy.

And that's the-- I call it the hand-waving heuristic definition of entropy that, to be frank with you, is what got me started with this subject because I was so unhappy of the way I was explained the subject that I wanted to study it more. It's funny. You hate the subject because you don't understand it. And then you become to love it because you want to understand it.

All right. But how does this definition match with our usual understanding? Because if I ask you what's heat, well, heat is the energy that is transferred between systems at different temperature, you would say. Well, we just said, no, heat is the energy that's transferred between systems at the same temperature.

So is there something wrong? In fact, there isn't. Because, think of the typical model that we adopt in heat transfer. Suppose we have two systems at different temperatures. And we put them in contact. In the region of contact, their initial equilibrium, if they had a temperature initially, as soon as they get in contact, in the region of contact, you get a non-equilibrium situation.

But we may describe this system as a composite of many smaller systems. In fluid mechanics, you would call them infinitesimal fluid elements. In a two-dimensional problem, you could have infinitesimal slices of your solid or body.

And then you may assume that-- we will return, when we do non-equilibrium, we return very much to this idea-- we subdivide our system in such a way that each local subsystem is still in a non-equilibrium state. But it is not too far from equilibrium. So it turns out that we can assume that this is what we do when we describe a temperature distribution in our solid.

Temperature distribution means that there is a temperature at each location. So that means that each infinitesimal element is close enough to a stable equilibrium state that you can assign the temperature of that stable equilibrium state. And the fact that the temperature distribution is typically, except extreme cases, continuous means that if you look at it from the small partitioning point of view, each element has a temperature, which differs only slightly from the adjacent element, and so on, by continuity.

So each lamina, or each element, is at a temperature very close to the temperature of the near, of the neighbor. And therefore, the interaction between them is an interaction in which there is exchange of energy and entropy and in which the two adjacent elements have almost the same temperature, which fulfills our definition of a heat interaction. So locally, it is a heat interaction at the local temperature. And then with the other element, it's another interaction at a lower temperature or a higher temperature and so on.

This describes what I just said for, say, a solid. So suppose we concentrate on these infinitesimal elements of solid or continuum in which the coordinate is only, let's say, one dimensional, coordinate is between x and x plus dx. So it's infinitesimally thin. And it is in contact with the element to the left and the element to the right. And for simplicity, let's just study the steady state situation here and make the energy balance and the entropy balance.

So if I make the energy balance to this lamina, I should put on the left hand-side the rate of change of the energy of the lamina and, on the right hand side, the net contributions of the interactions to which that lamina is subjected. So it receives Q dot. Now, I'm assuming it is a heat interaction. So it receives Q dot from the left. And it gives Q dot to the right.

If what comes into the left and goes out to the right is balanced, same rates, the energy balance says that the rate of change or the rate of accumulation of energy of my system is 0. So that property doesn't change with time.

For entropy, the entropy balance should be written this way. Left-hand side, the rate of change of the property, so the rate of change of the entropy of-- this is our system, the lamina. On the right-hand side, I have two terms. The terms having to do with the net entropy received by interaction and the last term is the entropy produced by irreversibility within the system.

So from the left, the entropy that is received, the rate with which entropy is received is Q dot over T. And T here is Tx, T of location x. From the right there is an outflow of entropy, which is Q over T. But here, the temperature is different. It's T at x plus dx-- one with a plus because it's entering, one with the minus because it's leaving. And that's the entropy balance.

So if we assume a steady state, steady state means the state doesn't change with time. The state is what? It's the properties. So none of the properties changes with time, including entropy. So steady state implies that dS/dt is equal to 0. Then using this expression, we can compute the entropy produced by irreversibility.

And we recognize here Tx and Tx plus dx. If I divide that by dx, that's an incremental ratio. So that's the derivative of T with respect to x. T squared at the denominator-- so this is the result. It says that the entropy produced by irreversibility is proportional to the heat that goes through divided by T squared and multiplied by the-- dT/dx is the gradient in temperature in the x direction with the minus sign in front.

So this tells us a few things. First of all, it tells us in which direction Q can exist for a given temperature distribution because the entropy produced by irreversibility can only be positive or 0 if we were in a reversible case. But it cannot be negative.

So it means that Q dot-- here, I have a T squared. So it means that Q dot must have opposite sign of the gradient in temperature. So the Q dot flows in the direction of decreasing temperature, which is, of course, what we knew, what Clausius told us in another way the other day.

The point, though, is that-- let's look at what kind of model we're doing by assigning a temperature here. It's really an approximation that we are making. So in the whole of heat transfer and fluid mechanics, when we make the local equilibrium assumption, it is an approximation, which is good in order to assign local properties like temperature, pressure, chemical potentials to the fluid elements.

But we should not take it too literally because, if we were truly in an equilibrium state, these things couldn't happen. And look at it this way. Let's say that this is the E versus S diagram of my system here, the lamina, the infinitesimal element.

Now, yeah, I think I have it bigger here. Now, so the state-- I draw the state of this lamina just a bit off the stable equilibrium state curve. And let's see what happens there. So this is the state. The lamina receives both energy and entropy from the left.

So that energy and entropy from the left that received from this side-- so the left-hand stuff-- from the left-hand side, there is a pull that tries to pull the state up, because it wants to receive energy, and to the right, because it receives an entropy given by Q dot over T. The net result is that the state is pulled in this direction. It wants to move there.

On the other hand, there is also an interaction to the left-- I'm sorry, to the right, which takes things away. It takes energy down. So it pulls down the same amount. So these are balanced. And therefore, the state will remain at this level.

But it pulls to the left a different value because the temperature is different. And here, at x plus dx, the temperature, I assume it's smaller, so this ratio, since it's a denominator. The smaller at the denominator means bigger. So it means that this pull to the left is higher than the pull to the right. So there is an unbalance.

And if there weren't entropy produced by irreversibility, this state would follow the unbalance and go backwards. So that is to say that I need this irreversibility to be produced locally in order to maintain the steady state of that fluid element.

But in order to produce entropy by irreversibility, I must not be at stable equilibrium because, at stable equilibrium, the system is happy. And it doesn't rearrange things in order-- it already is in the maximum entropy. There is no tendency to produce more.

So this is to say that there is a bit of a contradiction, or at least that we have to be careful in understanding what the actual assumptions are. This state is a non-equilibrium state. Otherwise, it couldn't produce entropy by irreversibility. But it is close to a stable equilibrium state. And therefore, we can use the idea of temperature and assign it to the fluid element.

But indeed, what it is is the temperature that would be reached if I took that fluid element and isolate it from the rest and let it relax to equilibrium because if I shut the interactions left and right, this non-equilibrium state will spontaneously move to stable equilibrium. And then it will have a temperature. And that's the temperature that we assign to this non-equilibrium state.

This is interesting because it is the local equilibrium model that we are used to using in fluid mechanics. But you can improve. And people are doing extensions of fluid mechanics treatment in which you deal with this little difference in entropy because maybe you can assign a temperature, but the entropy of this state is slightly less than the entropy of a truly equilibrium state at that temperature. And that difference in entropy does sometimes-- has an importance for certain applications.

OK. So now I want to talk about these very traditional ideas of heat engines, heat pumps, and refrigeration units, and see the energy and entropy that flows. And also, it gives us the opportunity to define what we mean by first and second law efficiency of devices like these.

So let's start from what we are seeing. So let's do it our own way. Suppose we take the Clausius inequalities that we have seen the other day and remember that these subscripts over the extreme inequalities indicate what the condition should be for the strict equality to hold.

And here, if you remember, we have a strict equality if the system is in a stable equilibrium state-- ends in a stable equilibrium state and it is a reservoir, so that the second derivative is equal to 0. So let's consider our system to be a reservoir at temperature TA. I dropped the subscript 1 because, for a reservoir, there is always one temperature for all states. And let's assume that also system B is a reservoir. So also for B here, I have an equal sign because I also assume that the final states are stable equilibrium.

All right. So then either this or that inequality-- if the two temperatures are different-- and here, we would like to consider reservoirs at different temperatures, even large differences-- there is no way that this left extreme can be equal to the right extreme. And therefore, somewhere, there must be some irreversibility, either in system A or in system B, so as to make this train of equalities and inequalities satisfied.

So it is necessary-- if I transfer energy from a reservoir to another reservoir at a different temperature, it is necessary that some entropy be generated by irreversibility in either one because there are no other systems around. But suppose we interpose a machinery between that exchange.

Well, in that case, it is possible to have things-- to operate without irreversibility, so without entropy production. This is the entropy balance for the machinery. It says that, well, if the machinery produces some entropy by irreversibility, it must be equal to the difference between what it puts out from what it receives.

And this is the energy balance for the machinery. It says that it can produce work if it can manage to give to reservoir B less energy than it receives from reservoir A. So we can assume that everything-- it is possible to assume that everything has no entropy produced by irreversibility, so no delta S irr in system, no delta S irr in system B, and also no delta S irr in system X.

In that case, from the entropy point of view, the machinery simply passes the entropy that comes from reservoir A and gives it to reservoir B. But it also recognizes that the machinery is made there just to recognize that, in order to pass that entropy to system B, it doesn't need to give it all the energy it received from A. There is an unbalance, the difference, which can be transferred out by means of an interaction in which there is no entropy transfer, work.

OK, so that's the idea of the heat engine, machinery that receives heat from a reservoir at high temperature. This is a heat engine between thermal reservoirs because you could have also heat engines between systems that are not reservoirs. I take a big piece of steel out of a steelmaking plant. And I want to recuperate the energy that it has before it cools down. That's a way of recovering energy from industrial processes.

And of course, as I call it down, the piece of steel decreases its temperature. And so it's not a reservoir. That doesn't mean we cannot compute also for that situation what is the maximum work that we can extract. But that's another situation. And for example, the maximum work we can extract in that case is not the Carnot coefficient.

Whereas here, if you do energy and entropy balance-- and here they are. I'm going quickly here. And I'm not going too into the details, just give you some ideas by following the flows of the entropy. But here are the full glory of the balance equations for the machinery, from which you can compute the work.

Here is the result. So the work that the machinery-- the useful effect that the machinery can produce is equal to a fraction of the heat that it receives from the hot reservoir. And that fraction is the Carnot coefficient between those two temperatures.

And then there is also a term which detracts. And that is proportional to the entropy that is produced by irreversibility within the machinery. It has a minus sign. So if the machinery does produce entropy, that will detract and will allow you to get less work than the maximum.

Let's view it from the point of view of entropy flows. Actually, maybe we can also do it in terms of E versus S diagrams. So this is system A, reservoir A. And this is reservoir B. And I'm extracting some energy. So I want to take this much energy out of system A.

Clearly, there are no states here. So I need to extract also some entropy, at least this much. But in order to extract that entropy, I need another system-- that's why I need the reservoir B-- that picks up that entropy. And so it will end up here.

It will end up here, provided-- since there are no states to the right of the maximum entropy, I need also to provide some energy. And that energy is this much. It's Q received by B. So the difference between this and that is the work. If I draw a line with the slope of reservoir A here, this is the work that I have extracted.

Actually, this is W rev because I have assumed that system B takes just barely the entropy that we need to-- that is being received by system A. So it flows-- the entropy comes from A. The machinery doesn't add because it's reversible, it doesn't produce additional entropy. It simply has to transfer it to system B.

And the energy that is required to transfer that to system B is less than QA. And therefore, there is a difference. And that difference can be transferred in an interaction where there is no entropy transfer, which is work. So this is the reversible operation.

If we have an irreversible operation, so if the machinery is irreversible, like most practical machineries, and therefore it produces some entropy, that entropy will also need to be disposed of into the environmental reservoir. And therefore, it will require more energy to follow.

So in the system B, I need to add not only this entropy, but also the entropy that is produced by irreversibility. So that is S irr produced in the machinery. And the machinery is called M. So system B ends up here. The amount of Q is higher. And therefore, the amount left, the difference, which is what will be transferred as work, is less.

Good. So we have seen it in various ways. Now, typically, one defines the efficiency. Actually, most of you probably remember that this ratio is not called the Carnot coefficient, like I'm calling it. But it's called Carnot efficiency, which is true in the sense that I can define an efficiency-- we are going to call it here first-law efficiency-- as the ratio of the useful work-- so the work-- divided by the energy of the resource that you have used. In this case, the resource is the hot reservoir, so the energy extracted from the hot reservoir.

So this ratio is the first-law efficiency. And the result of the energy and entropy balance shows that the Carnot coefficient is the upper limit of this efficiency, which is reached when S here is equal to 0. So the Carnot coefficient is equal to the first law efficiency for the reversible engine.

What is somehow inconvenient of first-law efficiencies is that usually when you say, something is 50% efficient, I would say, well, why aren't you doing better? There is 50% room for improvement. Not here though, because there is no way-- suppose you have TA is equal to 600K and TB is 300K. So the Carnot coefficient is 1/2, 50% That's the maximum you can do. There is no improvement. You cannot improve.

So it would be better to have to call efficiency or to-- so people have introduced the second-law efficiency, which compares what you actually obtained and put it in a numerator to the maximum that you could have obtained, given the constraints and the physical laws, so without violating anything.

So in that case, this ratio, for the reversible case, is 1. So it's 100% And so if the efficiency is 100%, there's no room for improvement. If it is not 100% or 1, it means that there is something that reduces that. And that something is the entropy produced by irreversibility.

So by thinking in these terms, this second-law efficiency allows you to identify the actual places in your machinery or power plant that are the sites where entropy gets produced by irreversibility because the higher the entropy produced by irreversibility, the lesser this efficiency, so the more room for improvement. And in fact, a lot of energy technology engineering is into improving this efficiency. That means identifying where the irreversibilities are and removing them or reducing them, optimizing from that point of view.

So let's do, even more quickly, the same idea, but for a refrigerator unit. It's again a situation in which I have two reservoirs, TA and TB. And I identify the environment as the system at a higher temperature now. And the other system, at the lower temperature is, for example, the refrigerator cell, the room that you want to keep refrigerated. And you want to keep it refrigerated. So since typically there are heat losses from the walls of this refrigerator, you need to compensate by removing heat. So the unit wants to extract heat from a low temperature, from a temperature from a reservoir which is at lower temperature than the environment.

So if we go on our-- do again the construction here, now I want my system B, which is the refrigerated room-- you want to extract energy. And as usual, in order to extract energy, you need to extract also entropy. So this is QB out. And this is SB out. So if I have this entropy going somewhere, I need to put it to another system.

Now, this system A, which is my environment, is there. And I would like to give it this much entropy. But in order to give it, I also need to give some energy, which is actually higher than this one because the environment is hotter. So it has a higher slope. So if I plot here the slope of system B, this is the energy that I extract from system B. But I need to give to A more energy in order for it to accommodate the entropy that I must extract from B. So this much is the work that I need to spend.

And of course, if the machinery is irreversible and it produces also some entropy by irreversibility, not only I must accommodate this much entropy, but I must accommodate even more. That's the irreversibility of the machinery, this much. So system A must go up there. And therefore, I need to spend more work. So this was W rev. And this match is W, say, irreversible.

Now also here, the Carnot coefficient or similar does play a role. Usually, in practice, when you buy a refrigerator, you want to know what the COP, the coefficient of performance, is, which is a first-law ratio. It's the ratio of the useful, the cooling effect, which is the energy you extract from the low temperature cell, to the work, typically electrical work, that you need to spend in order to do this.

And this COP has a highest value. And then there is a term, which is always positive. And that is bigger and bigger the more irreversible is your machinery. Also here, COP is typically a number greater than 1. It doesn't give you an indication of what the room for improvement is.

The second-law efficiency instead does. And again, we can define it as the actual useful effect divided by the best useful effect, the maximum useful effect you could obtain with a reversible machinery. That too has a maximum value equal to 100%. In that case, there is no room for improvement. And it's less than 1, due to the entropy produced by irreversibility.

The last of this series of traditional machineries is the heat pump. The heat pump is very similar to a refrigerator, more or less the same equations, except that now what switches is the position of the environment, of your environment, the environmental reservoir.

Whereas for the refrigerator you were extracting energy from something which is colder than the environment, in the heat pump, you want to put energy in a reservoir which is hotter than the environment. So now, the environment is system B. But the idea is more or less the same, except that the useful effect now is not the cooling of B, but is the heating of A. You want to heat up something, like the house, using a heat pump, which is nowadays been done worldwide, at least in places where you need heating in the winter time.

And so the useful effect is QA. Therefore, you define a different COP. It's called COP, but it's different, a different definition. And this time, you put in the numerator the useful effect, which is the heat given to the hot system divided by the work that you have spent in order to do it.

And again, the second-law efficiency is the ratio between the useful effect of your actual machinery and the useful effect of the reversible machinery, so that it would be equal to 1 for a reversible machinery. And it's less than 1 if there is entropy produced by your machinery here.

So since now we are talking about some practical aspects, let's talk about another chapter of thermodynamics that has to do with establishing the properties of substances at stable equilibrium. And let's see, this is an important chapter. Many scientists have devoted their lives in constructing the properties of substances.

For example, to stay here, Professor Keenan, in 1940 or maybe earlier, spent a lot of time developing the steam tables, which is the properties of water. So how do we measure properties of substances in stable equilibrium?

Well, much of the tools that we have is related to the conditions for mutual stable equilibrium that we have developed, like equality of temperature, equality of pressure, equality of chemical potentials. The good thing is that, if you have a thermometer-- what is a thermometer?

A thermometer is a system in which, in some way, you have put a scale in which you can read the value of the temperature. Then what you do, you stick it in contact to the system you want to measure. And you leave enough time so that you convince yourself that the two systems have reached mutual equilibrium.

And if you are convinced that they are in mutual equilibrium, then the theory says that the two temperatures are equal. So by reading the temperature of the thermometer, you have measured the temperature of system A, of which you may know nothing. So it's an indirect measurement of a property.

Similarly, the manometer-- you can construct a manometer so that you can read out the scale, the value here. You put it in equilibrium, mutual equilibrium with your system by drilling a little hole in the boundary with either a little piston or some moving interface, like here.

If you are convinced that they are in mutual equilibrium, reading the pressure of B gives you information about the pressure of system A. So this is one way of measuring it. Yeah, this is just to remind of that proof that I don't want to go into details of, but that shows why the pressure can be measured by measuring a force per unit area anywhere on the boundary of your system.

So you take the boundary of your system when it is in stable equilibrium, drill a hole, and substitute that piece of wall with the movable wall. And then you find a force per unit area that keeps that wall where the original one was. Once you've found that, you have measured the force per unit area that balances the pressure of your system.

And when you are in stable equilibrium, that force per unit area is equal no matter where you go and do this procedure, whereas off equilibrium, it can be-- you can always measure force per unit area. But it may be non-uniform, not equal everywhere. And there is no pressure because you are not in equilibrium.

Another kind of measurement that we can do is the so-called Joule apparatus, in which you input some mechanical energy in your substance, or in a piston-- or in a variable volume, or in a constant volume container. You put some energy in, wait for the system to go to a new stable equilibrium, and measure how much the temperature has changed for your system.

So Mg delta z represents the amount of energy that you have put in, in the form of work. So you produce a work interaction and put energy into your system, let it relax until it reaches equilibrium, so a new temperature, compute the difference between the new temperature and the initial temperature, delta T. This ratio turns out to be equal to the partial derivative of this property that we're going to define in a moment. And that's the property that we call heat capacity at constant pressure. It's a stable equilibrium state property. We obtain it from the fundamental relation.

There is one heat capacity that is equal to the same ratio when you do the experiment at constant volume. And there is another heat capacity when you do it at constant pressure. So let's start from the constant pressure because this gives us also a procedure to define the enthalpy and to get to this, the derivative that turns out to represent the result of these measurements. So it's important because it is the way in which you measure that property.

Let's do it starting from the fundamental relation in energy form. And this is its differential. So H-- in a moment, we will see that this H has a particular transform of the fundamental relation when we change variables. But for the moment, let's just take it as an abrupt definition. Let's say that we call H the sum of energy plus the product of pressure and volume. We call it enthalpy.

Then by taking the differential of this expression and recalling that the differential of a product is equal to pdV plus Vdp, where I see dE, I use the differential that I have written up here. So I substitute. And this is what I'm left with.

From this expression-- I can view this expression as the differential. So you see, the independent variables are under the d-- so dS, dp, dn. So this would be the differential of a function in which H is a function of S, p, and n.

And also, the coefficients of the differential are the partial derivatives. So for example, the T is the partial of H with respect to S. The partial of what? The partial of this function, so the partial of a function in which the enthalpy is expressed as a function of S, p, and n. So that's the temperature.

Now, in the business of measuring properties, we like to have instruments. So we have a thermometer that measures temperature. A manometer measures the pressure. There is no energy meter. There is no entropy meter. We measure energy and entropy indirectly through temperature and pressure and volume.

So let's do that also mathematically. So you look at this equation here and this other equation, and consider it as a system of two equations in which you want to eliminate the property that is hardly measurable-- difficult to measure, hard to measure, which is the entropy.

So for example, solve this expression, this function here as a function-- instead of T as a function of S, write it as S as a function of T. And then take that S and put it in the original function up there. You manage to find H as a function of T, p, n. So you change the independent variables to ones that can be easily measured, temperature and pressure.

So this new function-- and this is the way you have obtained it-- so we have a precise way-- recipe to obtain that function, if we start from the fundamental relation-- is-- of this function, you can take derivatives. For example, the derivative of H with respect to T is what we call the specific heat-- sorry, the heat capacity at constant pressure. And it is a function of T and p. So pressure and temperature, we can measure. Heat capacity we can measure with this instrument here. And so this is a fully measurable function.

A similar procedure we can follow to define the heat capacity at constant volume. So we start again from the fundamental relation. And notice that the temperature, which is the partial derivative of E with respect to S, is being a function of this variable-- I mean, a derivative of a function of these variables has the same independent variables. So it's also a function of S, V, and n.

And also here, play the game of eliminating the not so easy to measure property, entropy. So solve this as S function of T and substitute up there to obtain that the energy-- a new function in which the energy is expressed in terms of the independent variables, temperature and volume. These are things that are easy to measure because temperature you measure with the thermometer, volume you measure with the stick.

So the first derivative of this function, the partial of E with respect to T, is called the heat capacity at constant volume. And it is the thing that you measure with that other Joule apparatus at constant volume. So we retain that.

But we can also do this other procedure. We take the temperature, like before here, but now we make a system also with the pressure. The pressure is the derivative of E with respect to V. And being a derivative of a function with these independent variables, it also has the same independent variables.

Eliminate entropy also from these two. That results in a relation between pressure, volume, and temperature, which we call the equation of state. Pressure, volume, and temperature are also easily measurable stuff. That's the equation of state.

And the partial derivatives of this equation of state-- so the derivative of V with respect to T, says how much the volume of your substance changes as you vary the temperature, as you heat it up. So it's the coefficient of expansion. If you do it divided by V, it's the percentage increase in volume per given amount-- or given increase in temperature. And you can measure this when you do the experiment at constant pressure.

Or the second, the other derivative, the derivative of V with respect to P, it says how much the substance gets reduced in volume if I increase the pressure. So the reduction is minus delta V per unit of increase in pressure. And again, if I divide by V, it's the percentage reduction in volume.

So when you do the experiment, increase the pressure at constant temperature. This is the isothermal compressibility of the substance. Being derivatives of the equation of state, they are functions of T and P. And these are easily measured because it simply relates measuring changes in volume, measuring temperatures.

So the differential of the equation of state done at fixed amounts has these two coefficients, isobaric expansion and isothermal compressibility appearing directly here. There are other things that you can measure in other experiments.

For example, an interesting one is the speed of sound propagation. It should be an of here. Or the Joule-Thomson coefficient in the expansion of a gas in a throttle, which occurs at constant enthalpy. You measure the change in temperature over a drop in pressure. And it can be positive and negative. And that is related to the things, the properties that we have already defined before. And also, the Mayer relation shows that Cp, CV, alpha p, and kappa T are not independent. So you don't need to measure all four of them. You just need to measure three.

Let me skip that one for a moment. No, no, I need it. I need it. In order to measure chemical potentials, I do need first to show that the chemical potentials can be written as functions of temperature and pressure. Because you see, the chemical potential is defined as the partial of E with respect to n at constant S and V, but that way, it isn't easy to measure because of the S.

So mu i is the partial of E with respect to ni at constant S, V and all the other n's held-- well, I shouldn't say that, where the function that I am taking the derivative of is a function of S, V, and all the n's. However, when you view it this way, it's not easy to measure because I don't have an energy meter and I don't have an entropy meter.

So the trick is to change variables. And one way to do it is to define a function, which is called the Gibbs free energy. For the moment, think of it as just an arbitrary definition. So I say, define this energy minus TS plus pV. Write the differential. Use the differential of a fundamental relation in order to express dE. And here is what you are left with.

This expression shows that you can view this function G as a function of the independent variables that appear under the d of the differential-- so the temperature, the pressure, and the amounts. So G has as, say, natural variables, T, p and n. And since this is the differential of that function, the chemical potential can therefore be written now also as the partial of G with respect to ni.

And since it is a partial of G, which is a function of T, p, and n, it's also a function of just T, p, and n. So the chemical potential, we would like to measure it. It is very important to determine the properties of multi-component systems. But it cannot be measured directly. There is no chemical potential meter.

However, it can be measured indirectly via the definition of what we call the partial pressure of a component in the mixture. Here, the experimental setup is this. I have my mixture in which I have many components. And they are in a stable equilibrium state. They are at some pressure, some temperature, and they have their chemical potentials, and so on.

So what I do is to drill a hole in the wall somewhere of my system and substitute the wall with a membrane, a semi-permeable or porous medium, or a semi-permeable membrane, where only molecules of type I can cross. The others don't.

So I put on the other side-- I put on the other side molecules of substance i. And with a piston, I keep them there. And I measure the force per unit area that is necessary to keep them in mutual equilibrium. When I reach mutual equilibrium between this little system, ii, the double script i we use as a way to say that it is a pure substance. So in this little box, there is only substance i, whereas in the mixture there is substance i mixed with other stuff.

When we are in mutual equilibrium across this membrane, we have proved also the other day that the conditions for mutual equilibrium are equality of temperature-- so the temperature of system ii must be equal to the temperature of the mixture. And the equality of chemical potentials for the substance that can be exchanged. So the substance is i. And so I need that the chemical potential of substance i of the mixture must be equal to the chemical potential of the pure substance i just on the other side of a semi-permeable membrane.

OK. Here, I also put the functional dependence because I used what we just proved before, that the chemical potential are functions-- can be written as functions of T and p. And so these are the functions that we are going to use for this measurement.

So by looking at this equation, which is required by the condition for mutual equilibrium, we see that inside the independent variables are all easily measurable things-- temperature, pressure, and also this pii, it's the pressure of the system on the other side of the semi-permeable membrane. We call that pressure the partial pressure of constituent i in the mixture. It is a property of the mixture. And it can be measured.

And by measuring it, and by knowing how the chemical potential of the pure substance depends on-- so if I know this for the pure substance, I can infer from that measurement the chemical potential of the constituent in the mixture. This is how we characterize mixtures.

So here is a little summary of properties that we have talked about so far-- energy, entropy, also the volumes and the parameters that enter in-- the amounts of constituents that enter in the definition of our system. These properties are defined for all states, equilibrium and non-equilibrium.

Then we defined some other properties based on the fundamental relation for stable equilibrium states. So clearly, these are defined only if you have a fundamental relation. So they are defined only for stable equilibrium states-- temperature, pressure, chemical potentials, the enthalpy, the Gibbs free energy, the enthalpy because it's E plus pV and p is the pressure. Pressure is defined only for a stable equilibrium. Or the Gibbs free energy has the p and the T also. So it also is defined only for stable equilibrium states.

And then we also defined these four properties today-- the heat capacities, the coefficient of expansion, and the coefficient of compressibility. These ones also are restricted for equilibrium states. But they're even more restricted because some of those mathematical steps that-- for example, if I go back here, when I do this eliminating one variable, I can do that only if some derivative is not equal to 0.

So for example, if the partial of T with respect to S is equal to 0, I cannot invert that function because it's not monotonic. And this is what happens, for example, when I have two-phase states, like liquid and vapor coexisting. In that case, some of these functions are not defined or, which is the same, take up infinite values.

So we go back to here. Now, this also says that if we do our measurements and we can, for a given substance, or for a set of mixtures, develop or measure experimentally these functions, the alpha p as a function of T, p, and composition, kappa T, is a function of temperature, pressure and composition. The specific heat at constant-- I'm sorry, the heat capacity at constant pressure as a function of temperature, pressure, and composition and the chemical potentials as a function of temperature, pressure, and composition.

If I have all these functions, then, with these functions, I can reconstruct the fundamental relation. So I know everything that I need to know about the stable equilibrium states of that substance. And actually, the reconstruction is done through these relations here, for example, the energy.

These expressions for the energy here can be related to these properties in this way. So if I integrate from one temperature to another, from one pressure to another, this expression, I can get variations in energy. The entropy also is related this way. The enthalpy is related that way.

And these are general forms that are valid for any pure substance. If you also need to consider mixtures, then you need to generalize this to use the expressions where also dn appears. So in this way, we have a way to measure the fundamental relation of substances.

OK. Now, yeah. Yeah, we have five minutes. I can do this. I want to show that some of these function, like the enthalpy and the Gibbs free energy, are obtained as Legendre transforms of the fundamental relation. Legendre transform is a particular procedure that we can explain in this way.

Let's start with the function of a single variable. So suppose you give me a function of a single variable, like any function. But to simplify, let me suppose that this function is either convex or concave and monotonic so that I can invert and play with it.

So usually, we define a function-- I'll call it f of y, meaning that, for each value of y, I get a value of f. And as I move y, the function tells me how f moves. But there is an alternative. The idea of Legendre is that there is an alternative description because that function also has a tangent and has a line tangent to every point.

So this tangent is characterized by two items, one that we will call lambda, which is the angular coefficient or the slope of the line. And this other value here, that we call L, which is the intercept at y equals 0.

So the idea of Legendre is that you can-- if you draw, like it's sketched here, the slopes at every point of the line, you get a family of lines, the envelope of which is your original curve. Each line is characterized for a given lambda, for a given lambda by L. I change the point. So I take another lambda. Suppose I want this slope, this match. So I fix lambda. So say this is lambda 1.

Now, I fix lambda 2. And that gives me L of 2. So selecting a value of lambda specifies, selects the point in which the tangent as that slope, of the original curve. And therefore, when you place your line there, it also selects an intercept. So there is a relation between lambda and L. And that relation is the Legendre transform of your function.

The procedure runs this way, that you take the function, you write the equation for the partial, for the derivative. And then you define L by the geometrical construction. So it's the function f minus this distance here. And this distance here is equal to the horizontal segment times the slope, so the tangent of this angle, so lambda. So L is equal to f minus lambda times y. So it corresponds to that description.

And I think the time is up for today. So we'll pick it up from here the next time.