[SQUEAKING] [RUSTLING] [CLICKING]

GIAN PAOLO BERETTA: So today, I would like to finish the first part by saying a few more words about exergies and the allocation problems. That's going to be also useful for the homework. And remember that one of the things that we have touched upon is heating a bulk flow-- for example, heating water from condition 1 to condition 2, which therefore requires, by the energy balance, an energy, which is given by the flow rate, times the change in the enthalpy of the flow.

That may be understood or called heat, even if it is a bit improper, because that is not really a heat interaction. Or at least, it is a heat interaction at multiple temperatures as the temperature changes from 1 to 2 here. Nevertheless, if we agree on the meaning, we can call it heat.

And then the coefficient of performance of, for example, in this case a heat pump, that provides that heat by taking the necessary entropy from the environment because, in order to heat up, I also need to provide entropy. And if I take it from the environment, I avoid having a generation by irreversibility.

The machine needs some work to operate. And the ratio between the heat and the work that are provided is called the COP. So the COP plays the role of the first-law efficiency. But it can be higher than 1. So we call it COP. We don't call it efficiency.

It's a ratio of two energies, whereas the second-law efficiency is the ratio. You can cast it as either the actual COP over the maximum COP, which you would obtain if the machinery was reversible. Or you can cast it as the ratio of the exergy change or the exergy that you have provided to your bulk flow over the exergy of the resource that you have used-- in this case, work.

We have also seen that if I take h2 minus h1 times m dot outside of the parentheses and I recognize that we called it QA, the remainder is a Carnot coefficient-looking combination that if we define h2 minus h1 over s2 minus s1 as the logarithmic mean temperature or the equivalent heat temperature that provides the same ratio of energy and entropy, then you can write it this way.

And here, you recognize that QA over W is COP. So the second-law efficiency is given by COP times the Carnot coefficient. And what is the maximum COP? Well, the maximum COP is when the second-law efficiency is equal to 100%, reversible machinery. So you set this equal to 1. And therefore, COP max is the inverse of that Carnot coefficient.

So we also played with some numbers because this is an important topic. And it is a way in which we consume a lot of energy. So if we want to improve our ways of using fuels or any other exergy resource-- natural resource, for example, nuclear and solar and so on-- we want to know the efficiencies.

And so here we gave an example of heating water in an industrial setup. Typical numbers could be from 60 to 120 degrees C. And then if we compute that Carnot ratio-- and remember that here also we need to make explicit the assumption of the environment that we have available when we compute that because that makes a lot of difference, especially for small temperatures and temperature differences.

So here, for example, if I take 300 K, here's the number. The Carnot ratio is 17.2%. And its inverse, which is the maximum COP for the heat pump therefore is 5.8. So 5.8 means that I spend 1 kilowatthour of energy and I deliver 5.8 kilowatthours of energy to my stream.

If I go to lower temperatures, like in residential heating from 20 to 60 degrees at the same environment, 300 K, which is like summertime because it's 27 degrees C, in that case, the Carnot coefficient is 4%. So you take the inverse of 4%, it gives 25.

So that means that, in principle, if you had a reversible heat pump with 1 kilowatthour of electrical energy, you provide 25 kilowatthours of heat, whereas, in an electric boiler, for 1 kilowatthour of energy, you provide 1 kilowatthour of heat or maybe a little less because maybe some is lost to the insulation of the boiler.

Then we also argued that the current way in which we use fuels, namely burning them in a flame and then using the hot products of combustion to heat up a working fluid of some thermal cycle, if we want to improve on that, the efficiency of these and go beyond the current, say, 64%, which is obtained as the product of an about 75% efficiency of the combustion of the flame and an 85% efficiency of the thermal cycle, you need to improve on these two efficiencies.

But even if you improve the thermal cycle to 100%, you're still stuck to the limit of 75%, say 80% for the flame. And we've said we've seen that history tells us that we are, on our learning process, heading towards higher efficiencies than 80%. And so the only way we can reach them is to find alternatives to the combustion in flames, the oxidation of the fuel in flames.

And we also said that when we do chemical reactions and combustion in a little more detail, we will see this diagram. And we will see that the flame goes this way. And that generates entropy by irreversibility, whereas if you are in a fuel cell or more able to control this process, and while the system spontaneously wants to go from fuel to products of combustion, you manage to extract also some energy, like in the fuel cell, then you may reduce the entropy produced by reversibility and your efficiencies can be higher, like in some examples here.

So usually, separate production of electricity-- we produce electricity in facilities, power plants, that use our fuel. And remember, we said that, for the moment, but also for typical applications, it is fair to approximate the exergy of the fuel by its heating volume.

So energy and exergy content are very similar, of the order of plus or minus 2%, depending on the hydrocarbons. So this is a fair approximation in practice. So you use this fuel. You burn it. You obtain these products of combustion. And then you transfer the heat from the products of combustion to a working fluid of the thermal cycle.

Then, of course, the products combustion must be exhausted to the atmosphere. And we are all concerned about pollution that comes from these exhausts, not only the global pollutant, CO2, carbon dioxide, which is a pollutant only in terms of playing a role in greenhouse effect, as we all know, but also other products of combustion, like NOx, so the various oxides of nitrogen, which can produce acid rain and other various effects.

So you need to control what gets out there. And typically, what gets out there is at relatively high temperature, say maybe 110, 140 degrees Celsius. This is when you don't want the water that is in the products of combustion to condense. That is to avoid-- because some fuels have some sulfur content. And water with sulfur makes sulphuric acid. And that's corrosive. And you want to avoid that.

But you can also have condensation. So if you can use higher level materials that can sustain corrosion, you can also condense part of the water that is produced by the combustion process. In that case, you extract a little more energy.

And then we talk instead of a lower heating value, it's actually you're exploiting, getting closer to the higher heating value or somewhere in between. We'll see some details about this. But here, the idea is that this energy is transferred to this thing and to this working fluid. And then the thermal cycle provides work.

And of course, since you're extracting not only energy, but also entropy, the thermal cycle must discharge that entropy to the environment, which is, at the moment, still considered a free way of getting rid of entropy. Although, some places we are talking about, of course, you need authorization to do that. So that is equivalent to not being exactly for free, not anymore. In other words, we cannot use the environment as a thermal dump for free anymore.

OK. First of all, efficiency here, we have only one product, whose energy content is W and only one energy source, which is the fuel. Its energy content is Q. So that's the first-law efficiency. And typical first law efficiencies, as we said, could be, yes, the best available technology could be maybe 65%. But the average efficiency of a national lot of power plants, well, it varies from country to country, of course.

For example, I think that in Italy is between 42% and 45%. The second-law efficiency is the ratio of the exergy of the product to the exergy of your fuel. Now, considering that the exergy can be approximated to the energy of the fuel, you see that, for this particular case, the second-law efficiency is equal to the first-law efficiency.

So indeed, if you are at 65%, the 65%, the margin for improvement is 35%. We only have 35% to go to get 100%. And remember that second-law wise 100% is not impossible. It's the upper limit. It's what you would have for reversible machinery. So the message is here that, for this particular case, eta 2 is equal to eta 1 approximately.

Now, when instead of producing electricity, we want to heat up something-- for example, here, a simple case of heating up a room at some fixed temperature or maybe heating up water to make it boil at some temperature, for example, here, 120 degrees, some pressurized steam production, which is very common in industrial processes for material processing and so on.

So now, the first-law efficiency is the ratio of the heat that you produce, that you deliver. So this is your final product over the energy of the fuel. The second-law efficiency instead is the ratio of the exergy of that heat. So it's the heat multiplied by the Carnot coefficient divided by the exergy.

Then again, we use the approximation that the exergy is equal to the energy content of the fuel. And therefore, we recognize this ratio here is eta 1. So in this case, the second-law efficiency is equal to the first-law efficiency times the Carnot coefficient.

So for example, if you want to produce steam at 120 degrees and you're in an environment at 283, you compute and you have a boiler that consumes, for example, natural gas. And it is 95% first-law efficient. So eta 1 is 95%. It means that only 5% is lost to the flue gases through the stack. And that means, so you've got the 95% times the Carnot coefficient here makes about 27%. So in that case, the margin for improvement is much higher, like 73%, to go to 100%.

In some sense, we should say that if this is representative of our typical way of heating up water in industrial processes by using fuels, the fact that, for this technology we are only 27%, whereas for power production we are 65% means that we are at different levels of maturity of these uses of natural resources for these two different technologies and products.

Most of the times, we-- many times, the burner doesn't have to heat up something at constant temperature, like when you boil something, but needs to heat up, for example, water. Again, for residential purposes, typical numbers are from 20 to 60.

And so here are these again. We have that, since the temperature is changing here, we can define a logarithmic mean temperature, which is the temperature that enters in the Carnot coefficient. And again, the second-law efficiency is equal to the first-law efficiency times the Carnot coefficient.

The typical number varies depending on what temperature T0 you choose, so depending on whether you are winter or summer. So for example, if you are in the summer, 25 degrees C is to 298 K. A residential domestic boiler, which has an efficiency of about 85%, first law, gets a second-law efficiency of just 4%.

Wintertime, if outside is at 0 degrees Celsius, it's freezing, then it's 11%. For an industrial boiler, the efficiency is a little better. First-law efficiency, let's say 95%. And if you go from-- yeah, OK. Maybe this is not true. This should be a 16%. Probably these numbers I think I did that from 60 to 120. Well, check the numbers if you are interested. And it gives a 12% in the summer and 19% for second-law efficiency during the winter. So there are ample margins of improvement.

And one of them is cogeneration, as we said. Produce with that fuel electricity, and then use your low temperature need-- a low temperature heat that is needed as a dump for entropy. And therefore, this becomes a second product, or a byproduct.

The second-law efficiency then has, as the numerator, the exegies of the two products-- work for the exergy of the work, of the electricity, and heat times its Carnot coefficient for the exergy of the heat divided by the fuel. And again, this is the same thing, where we highlight that the temperature-- if the temperature of what you're heating is changing, you need to put in the logarithmic mean temperature.

You can also do the same kind of calculations for refrigeration because, often in industrial processes, but also in air conditioning, residential air conditioning, you need to cool down. For example, air conditioning, you need to cool down a working fluid between 12 and 7, from 12 to 7 degrees C, typical.

So you can define a COP of the refrigeration, which is the heating load, so the heat that it takes away from the working fluid divided by the work that you have spent in order to run the machinery, typically compression cycle or refrigeration cycle, but not necessarily.

So this is the COP. The second-law efficiency is-- well, you can view this as minus QC times the Carnot coefficient. And again, the second-law efficiency, therefore, is the COP times the Carnot coefficient. And for typical values, I mean, for an industrial refrigerator for which the COP is about 5, which is relatively high, it means that you spend 1 kilowatt hour and extract 5 kilowatt hours of heat from the cooling-- as the cooling effect.

So 5, you multiply by the Carnot coefficient for those temperatures at an outside temperature of-- what is it-- 30 degrees C. And you get a second-law efficiency of 36%. Not bad. At least compared with heating, it seems that, with cooling, we're doing better.

In fact, the machinery for cooling is, as you know, the same as the machinery that we use for heat pumps. It requires more investment, more materials. And it's more sophisticated than just plain burning something and using a heat exchanger.

Now, people have tried also the simultaneous combined production of power, heat, and cooling. It's called trigeneration. You have three products. And actually, this considers also the fact that you may have-- that you may use, as a possible resource-- sorry, this is the cooling effect. This is the cooling effect. So this uses as a resource only the fuel.

And therefore, you have three products. And here is one of the problems. It's not so easy to define a first-law efficiency because you have to put a numerator apple and oranges. So you have to put heat, work, and cooling. So they are different animals. And they shouldn't stay together in a numerator.

But you could define separate efficiencies, provided we have a way to allocate the fuel consumption and assign a fraction of it for each of the products, which is the idea of this allocation that we're now getting to refresh again.

So you see, every local area that could be a nation-- for example, here, I've put some numbers and the flag for Italy. And if you're interested in-if you have a preferred country, you can do this table. It would be interesting, in any case, to search and to see, for example, for separate production, one thing is to consider what is the average national efficiency. And one is the efficiency of the best available technology.

And then you have the same for combined heat and power. And you can do also the same for when you hybridize your use of resources by using some that are fossil fuels and some that are renewable resources. And of course, each line is for what product you are interested in-- so electric power, residential heat, winter, summer, industrial heat, cooling, and so on.

The list is long because energy products-- you could also consider the production of materials. For example, aluminum from the ore-- bauxite or whatever it is-- is a very energy consuming process. And so talking about efficiencies is important. And also doing cogeneration is also a way to save energy, so use better our natural resources.

And for each one of these technologies or products, energy products, we can also study where we are in the learning curve. And as we've seen, this is the learning curve for power production. If we did a learning curve for heat, we would be just about here between 10% and 20%. Cooling is between 20% and 30%. So the curves would be shifted.

And probably also the characteristic time could be different. But in any case, you see, it's not in the matter of just a few years. It requires many years to mature a technology. So that also carries the message that if you are in the energy business, or if you want to listen to a politician, you have to be careful because nobody can promise results in short times.

So that's another interesting story. So that brings us to the problem of allocation. As we have already discussed, in a cogeneration facility, it amounts to defining these coefficients alpha that are the fractions of the fuel that we think are used for the two products, that we assign to the two products. And we've seen that this assignment is a bit arbitrary. There is no law of physics that tells us how to do it. And each one has its pros and cons.

In particular, in order to evaluate these, it is interesting to see these primary energy savings because cogeneration does allow you to reduce the overall fuel consumption than if you did it in separate production facilities. So there is a savings. And the problem of these alphas is how you allocate those savings to the two products, heat and work.

And once you have chosen those alphas, you can define the COPs and the partial efficiency of your work and of your heat production. And as we said, this topic all started when the COP of heat production became important in determining the energy efficiency of buildings, which, in turn, determines the value of these buildings. So this has an economic impact.

And this incremental electricity-centered allocation method, which was assigning all the energy savings to the production of heat, is what triggered the need to do something better because that is unfair with respect to other people who would produce heat by just burning the fuel.

So typically, one would define these reference efficiencies for the separate production facilities, defined by some authority, and then define this coefficient of allocation as the weighted sum of what I would consume to produce that same amount of electricity in separate production facilities.

At least, this method has the advantage to split evenly the primary energy savings between the two products. So if I say 20%, I assign a 20% improvement to the efficiency of work and a 20% improvement to the efficiency of heat.

The people that are really fond of thermodynamics and would like to solve every problem with thermodynamics insisted for a while that you should use the exergy method, which takes as reference the reversible process because, after all, that is the ultimate target that we should be heading towards.

However, the problem is that, as we've seen in the learning curve, heat and work technologies have not the same level of maturity. And therefore, the distance of where we are from where we could be with reversible machinery, which is the exergy target, is very different, like maybe 35% for electricity and maybe 80% or even more for heat.

And this gives again too much advantage to the heat because the weight with which the energy savings would be split between work and heat would be proportional to that margin of improvement. And in fact, if we look at the numbers for this example here, we find that we would have a COP of 200, which is better than the 350 of the electricity-centered method.

But with more realistic reference efficiencies, you would have much more reasonable numbers-- I mean, lower numbers, like 92, maybe 96% for the COP of residential district heating, which is good because it's better than, say, the typical 85%. And also, it gives a more fair split between work and heat.

Now, the homework doesn't call you to do anything about this method of local area because that has not yet been accepted or incorporated in any of the standards. It's just an idea. And nevertheless, it's interesting to say that essentially what the local authority should use, according to our suggestion, is as reference efficiencies the average efficiencies of the local area, including the combined heat and power production facilities.

That way, if your combined facility is, like in this case, more efficient than the reference, then it deserves some incentive, or at least a clap, because they are doing better than the average in the local area.

So one criterion also for either giving incentives or giving authorization to make a new power plant is so that it meets a higher efficiency. It has a higher efficiency than the average. And therefore, in turn, it will higher the average efficiency of the area. So that would be beneficial for everybody.

The converse is when we do hybrid power plants. And in this case, we are using, in this paper, not cogeneration, but just power production, only power production. And instead of using just fuel, you use fuel and integrate that fuel with some renewable, like solar energy or vice versa.

Instead of having just a renewable, just solar energy heating a power plant, like those power plants with mirrors that we have said the other day, and you can look it up, there are a few prototypes in California, in Spain, in Italy, and probably other places, too.

Nevertheless, the fact that, of course, solar energy is not always available, and therefore you need to either make some storage in order to have it function continuously, or you could integrate with fuel for when-- to compensate, when there are clouds or at nighttime, so there is no solar energy available.

In this way, you may have advantages, both from the point of view of efficiency-- so it's more stable input for your power plant-- and also for the cost because the investment is going to be diluted over more hours of operation. So it is important, in this case, also to determine these fractions, the betas, the fractions of the product that can be understood as being the product of the fossil or the product of the renewable part.

So if I could identify what fraction of the electricity produced is considered renewable, this would be at the same level as, say, photovoltaic energy because photovoltaic energy is like a separate production from solar to electricity.

And so there is no reason why, if the country decides to give an incentive to photovoltaics-- there is no reason why they shouldn't give also an incentive to a hybrid facility, at least in as far as the fraction of electricity that is recognized as renewable because, in the end, it turns out that these facilities, hybrid facilities, have higher, slightly higher efficiencies than photovoltaics. So if photovoltaics is like 15% efficient, these facilities may go over 15%. And so it may be a better way of using solar energy for electricity production.

So also here, at the beginning, people thought of assigning all the benefit of the hybridization to the renewable aspect. But then this would be unfair because these power facilities, hybrid facilities, would get the incentives even if they don't deserve it. Because part of the savings made by the hybridization, should also go to the fossil line of the power plant.

So also here, a reasonable way is to use a reference production. So it would be the weighted-- the fraction of how much electricity you would produce with that fuel in a separate production facility. And the other is how much electricity you would produce in a solar facility. And these weighted ratios are balanced. But of course, somebody has to define what reference efficiencies to use.

And again, there is this consideration of the exergy method that would provide 100% as the target, the reversible target, and 93% for the reversible target in the conversion of solar energy into electricity. But these targets are very far from the actual level of average efficiencies.

And therefore, it is dangerous to use those as references. It is better to use as references something fixed or, again, something based on a local area, so the average values of the partial efficiencies in the local area, so that, again, also here you could argue that who deserves the incentives, the economic incentives, are only those who improve somewhat the average usage of those resources in the local area.

So for the numbers, here, there is an example. Yeah, I think I skipped one. I removed one slide in which it was saying-- yeah, here it is. The separate production for solar, that is typically, say, average of today for photovoltaics is 15.3%. And here, we use the 38% map. Maybe we could have put also 42%, maybe also 45% today for the separate production of electricity from fuels.

Now, here is the hybrid facility. And these numbers define the relative role of hybrid production in the local area. For example, this says that, of the overall electricity, 45% is hybrid and 10% is separate solar, so like photovoltaics.

And then by using these self-tuned average separate local production references, here is the numbers. For example, it would say that this hybrid facility improves the efficiency of production from solar from 15% to 18.7%. The exergy method would have said that the improvement is to 35%, giving therefore a lot of credit and therefore very high incentives. And the fuel centered even higher. It's nonsense.

So if you happen to end up working in one of these agencies that define regulations and that keep following the evolution of local areas and the improvements, you have to be aware of avoiding wrong numbers that would change the direction of technologies or investments not where you want it to be going. Because these numbers are in particular, the laws that determine incentives based on these numbers determine the choices of the companies where to invest in what.

All right, so with this, I think I have said a little more about this problem of allocation. And if you still have some questions, maybe this is the time-- for the homework, for example, maybe this is the time to ask. If it is all clear, then OK. In any case, if you need help, I'm available in the office. Just email me. And we can set up an appointment or just chat by email.

OK. Yeah, because now I want to move to the second part of the course. This was an initial slide, you remember, where we said, in the second part of the course, we're going to deal with chemical potentials and multi-constituent systems.

In part, we have already discussed-- these are stable-- A lot of this is played with stable equilibrium states. And we said a lot about the properties of stable equilibrium states. And in fact, in the next few slides, which are full of formulas as usual, I'll just review quickly the things that we've already said that are relevant to the applications that we want to focus on next.

So this part is divided into three other parts. The first one is defining properties of mixtures in a single phase. So we'll have to talk about partial properties, define what they are, define some ideal mixture. And here, I should also add another topic, which is ideal solution behavior.

We will talk about osmotic pressure. We will talk about the minimum work for separation of a mixture into its components or the maximum work that you can extract from mixing if you don't do it irreversibly. And then yeah, osmotic pressure and the so-called blue energy, and then also the problem of stratification-- so what's the composition in the air at various heights.

Then there will be a second part that will deal with liquid vapor equilibrium or, say, two-phase states for mixtures. And the third part, which deals with systems or mixtures with chemical reactions. Most of it is covered-- is still covered-- sorry, it's covered by the book here.

So here is a dense summary of things that we have seen. You remember, we defined these characteristic functions starting from the fundamental relation of the stable equilibrium states and performing the Legendre transform of some of its variables or all of its variables. We defined alternative ways of describing the properties of stable equilibrium.

And among these Legendre transforms, we defined the F, which is the Helmholtz free energy; G, which is the Gibbs free energy; H, which is the enthalpy; and Eu, which is the Euler free energy. They are all related like this. Of course, where you see this, that means the summation of the products of the various constituents. So we already set up for dealing with mixtures.

Also, this Euler free energy is a function of temperature, pressure, and chemical potentials. So that means that you can measure it by appropriate-- mutual equilibrium of your mixture with an appropriate environment of which you know the temperature, the pressure and the chemical potentials because essentially the value of the Euler free energy of your mixture depends only on that.

So once you've fixed your reservoir in a completely open situation in which the system can exchange energy, therefore temperature equality with the reservoir, pressure-- I'm sorry, volume, therefore pressure equality with the reservoir and it can exchange also all constituents with your reservoir, so all the chemical potentials of your system for each substance must be equal to the chemical potential of the reservoir of the corresponding substance.

And so that provides ways to do these measurements of this Euler function. Of course, the Euler function is important, as we emphasized, for small systems. It's also important for large systems because, for large systems, it is identically equal to 0 as part of the result of the simple system model in which we have seen that the refraction effects at walls are not important.

And therefore, for example, the work associated in placing a partition in your system or the entropy produced by irreversibility if you remove a partition, become negligible for large amounts. And so in that case, since the Euler free energy is related, as we have seen, to that work and to that irreversibility of placing or removing partitions, in the limit of large number of particles, that goes to 0.

And that gives rise to the so-called-- I mean, what is known as the Euler relation. And also, if you subtract the differential of the Euler relation from the Gibbs relation, which is the differential of the fundamental relation, you get this other relation between differentials that is called the Gibbs-Duhem relation, which we already used when we did, for example, the Gibbs phase rule.

Now, the various forms, the various differentials of the fundamental relation or the Legendre transforms of it-- Helmholtz, Gibbs, enthalpy-- so this expression for the differentials-- are useful in order to identify, just by inspection, what are the natural variables of these functions.

So for the energy form of the fundamental relation, the natural variables, as we know, are S, entropy, volume, and the amounts of constituents. And the amounts of constituents can be written in terms of mole fractions, this way and also, again by inspection, you can infer immediately what the partial derivatives of this function are with respect to the various natural variables.

For example, T is the partial of E with respect to S. Minus p is the partial of E with respect to V. The chemical potential-- and this is important-- when viewed this way is the partial of E with respect to n. And being a derivative of this function here, it is viewed as a function of the same variables, S, V, and n.

Then you do the same also, for example, for the same-- let's go down here to the Gibbs free energy. The Gibbs free energy has this form of the differential. So you identify its natural variables as being temperature, pressure, and the amounts. And the partial derivatives, minus S is the partial of G with respect to T. Volume is the partial of G with respect to pressure. The chemical potential is the partial of G with respect to n.

And this way, the chemical potential is viewed as a function of T, p, and n. It's the same chemical potential. We're talking about the same system in a stable equilibrium state. But you can view the chemical potential as a function of different variables because the game of the Legendre transformation is to change from not readily measurable variables, like the entropy, to more readily measurable variables, like temperature, pressure, or for the Helmholtz free energy temperature and volume.

The enthalpy doesn't gain much because it still has the entropy there. But the enthalpy is important for bulk flow interactions. And that's why we keep it in play. Now, of course, this is that summation. But when we have a single substance, so when we have a pure substance, we have this same set of equations.

This is valid, in general, so including small systems. It's the same as two slides before, only that we've written this as simply mu and n, only one substance. Or you could call it one. Or actually here, we are going to use the double subscript as a convention to denote pure substance. So if you see a double subscript, it means we are referring to pure constituent.

So in the large number of particle limit, so the simple-system approximation applies. And we still have the Euler relation. The Gibbs-Duhem relation simplifies and can be viewed as essentially the differential of the chemical potential of the only substance that we have.

So you see that the chemical potential is a function of T and P. Let's see. Yeah, here, I think I made a mistake in these-- let's see-- In the limit-- In the large n limit, the chemical potential loses its dependence on the amounts. OK, here it is written correctly. Oh yeah, OK, here, I did take it away. Fine.

So the chemical potential is not an independent property. Once you fix the temperature and the pressure, chemical potential is a function of T and P. So that fixes also the chemical potential, whereas, for a mixture, the phase rule, depending on how many phases you have coexisting and so on, some chemical potentials can be changed independently, not for the pure substance.

And in fact, if you have, for a pure substance, two phases, you have one relation like this for one phase, like liquid, and another relation, like this, for the vapor. And if they coexist, the two must be equal. And therefore, temperature and pressure are not even anymore independently variable, like when you have a single phase.

We will see that chemical potentials play an important role for mixtures because they determine the properties. And they also play an important role in determining the condition for mutual equilibrium. So they are really our focus. For the pure substance, notice that, due to the Euler relation, the chemical potential is also equal to the specific Gibbs free energy. So the Gibbs free energy per unit mole, g, is capital G over n.

Now, in the simple-system model, for a mixture-- so this is the simple-system model-- G is equal to that summation. When you have only one, that summation becomes just one term. And therefore, you see that, if you take g-- so it's mu11 n11 divided by-- let me put 11 here. So that's mu. So that proves that, in that case, the Gibbs free energy molar. So that's g11 is equal to mu11. Only for a pure substance.

So how do we measure properties? Well, in order to measure, we said that the chemical potentials are central because they determine, for example, the Gibbs free energy, which is a Legendre transform of the fundamental relation. And therefore, you can extract all the information from it, of course if you know it as a function. So you need to know not just one value, you need to know how it varies with temperature and pressure. You need to know all these functions in order to characterize your mixture.

And the chemical potentials are the key of the game. And the way you can measure them is by a manometer, by measuring the partial pressure. So you need to develop rigid, semi-permeable membranes capable of keeping the molecules-- all molecules in the mixture except one inside the mixture and allowing only the molecules of one type to cross.

Once you have identified a membrane like that, you just wait for mutual equilibrium to occur, and then measure this partial pressure. And then as you remember, the condition for mutual equilibrium is that the chemical potential of constituent i in the mixture must be equal to the chemical potential of the constituent on the other side of the membrane through which that substance can flow.

And we call partial pressure that pressure at which that occurs, the pressure of the pure system so that that's the meaning of the double i. And so this equality makes the-- yeah, OK. Here, I kept because, for small systems, you also have this dependence, even for the pure substance.

But for large amounts, that drops. And then you see that you can solve this equation and evaluate the partial pressure as a function of the other variables, which is temperature, pressure, and the amounts in the mixture, and the amount in this pure system on the other side of the membrane. But the absolute amounts would drop out for large n. So that dependence is only through the relative composition of your mixture, so the percentages of how many molecules of each type I have in my mixture.

And again, here, I use this relation, which is also important to remember, namely that therefore, for large n, the chemical potential of the constituent in the mixture is equal to the chemical potential of the pure component evaluated at the temperature and the partial pressure of the mixture.

And the chemical potential of the pure component is given by the Gibbs free energy. And the Gibbs free energy, if you remember, is also written as H minus TS. So what we are saying is that chemical potential of a component in the mixture can be written as this. But since this is g, it can also be written as h-- I'm sorry. This is muii-- hii at T and the partial pressure minus T sii at T and pii.

And these, with double i, are the properties of the pure substance. So a good part, but not all of the properties of the mixture are determined by the properties of the pure components. In fact, we will define some behaviors that we will call ideal, which are simplified versions, simplified models in which all of the properties of the mixture are determined by the properties of the pure components.

That is not to say that most real mixtures are not ideal in the sense that we will try to define. But the ideal mixture model, or the ideal solution model, are a good start. And then the typical procedure is just to start with an ideal description. And then since my actual mixture departs from ideal, you describe the departure from ideal. We are going to call those excess properties.

Now, a first step towards the construction of properties of a mixture from the properties of the pure components is to define-- I think we've already done it. Yeah, we defined already the partial properties. The way we did it was to write the differential of the expression that-- you see, this mu i is also, as we said, a function of T, P and the amounts.

So we write the differential of that. And then we use those Maxwell relations. That allows us to-- for example, this partial derivative of u with respect to T, which is the coefficient of dT in this differential, we recognize that, except for the minus sign, it is equal to the second derivative of G, of the capital G, of the Gibbs free energy with respect to T and with respect to n because the chemical potential is the partial of G with respect to n. So this is the second derivative.

But then due to the reciprocity or Schwarz theorem about second partial derivatives, this can also be viewed that you first do the partial of G with respect to T, and then with respect to n. So the partial of G with respect to T is minus S, as we can see from here. Partial of G with respect to T is minus S.

So by writing the differentials, we go and watch by inspection what these partial derivatives are. But also, we should remember, I mean, we could remember by heart these partial derivatives, at least this and that. In any case, this says how much the entropy changes while keeping temperature and pressure fixed and also the various amounts.

I add a little bit of one substance. This is why it takes the name partial entropy. It's the contribution of that constituent to the property of the mixture. Then we do the same. We did the same for these other partial derivatives, which is the coefficient of the pressure, which is here.

It can also be viewed as a second partial derivative of G. And therefore, in this case, it's the partial of the volume with respect to n. So it says how much the volume changes, increases, if I add a little bit of substance i while keeping temperature, pressure, and the other constituents fixed. And that's called the partial volume.

Also here, we have the expression for the differential. I have to take care also of the differentials of the n's here. So I have a summation because I have many n's. I have these partial derivatives of the chemical potential of one substance with respect to the amount of another substance.

And the reciprocity of second order derivatives tells us that there is a reciprocity in this relation. And for shorthand in what follows, I'm going to denote these partial derivatives as mu i comma j or mu j comma i. So the comma i means partial with respect to ni.

For example, this is the Gibbs relation, the differential of the fundamental relation. I can compute the partial energy of constituent i because I can take formally-- I mean, don't tell the mathematicians. But if I take these expressions here and I divide by delta partial n, partial ni, so I divide through-- so that becomes that d divided by dni is equal to T times dS divided by dni.

But that dS divided by dni is the partial entropy. Then I have dV divided by dni. That's the partial volume. And dn divided by dni is 1. dni divided by dni is 1. So that leaves me with just the chemical potential. I mean, it's 1 if the i I'm dividing is the same as the n. It's 0 if I'm dividing one by the other because they are independent.

And so this is how we prove-- I mean, you can do it better. But this was just a game because sometimes proceeding formally is helpful to go fast and do some checking. In any case, so this is the expression for the partial energy of a constituent. And you can play the same game using the differential for the enthalpy to express the partial enthalpy of a constituent.

What is important here is that all these partial properties-- entropy, volume, energy, enthalpy-- are related to the chemical potential-- you see the chemical potential-- or partial derivatives of the chemical potential, either with respect to T or with respect to p.

So that means that, if I have this expression here, I can determine, by just mathematical manipulation, all the partial properties of the constituent in the mixture. So from this one, I get si, vi, hi, ei. And what do I do with them? Well, this next slide is to show that with them you can compute the overall properties of the mixture.

So here, I do it again for the general case. And then I look at the large number of particles limit. Essentially, we can take the expression for the Euler-- this is one way of doing it, of course. There are many different ways of getting to the same result. For example, in the book, there is no discussion about the Euler free energy. And so you find a different derivation starting from just the value in the large limit, large number of particles.

In any case, I start from the expression for the Euler relation, which is a function of T, p, and mu. And then I substitute inside the mu here this expression here so that it becomes a function of T, p, and n. And then I take the derivatives of this with respect to these independent variables.

Of course, we need to do some chain rule because here we have a function of a function. So for example, the derivative of Eu with respect to T gets one contribution from the T that is here, this T here. And that's the derivative with respect to T done when I think that the other variables-- so let's say, loosely speaking, at constant p and constant mu. So I put that p and the mu here.

Plus, there is also a contribution to changes in temperature through the chemical potentials. So that adds the partial of u with respect to the chemical potentials times the derivative of the chemical potential with respect to temperature.

Now, it turns out that if we look at the expression for the differential of the Euler free energy, which is this one, by inspection, as usual, we can extract the values of the partial derivatives. For example, minus S is equal to partial of Euler over temperature. Volume is the partial of Euler over pressure.

The amount of constituent is the negative of the Euler with respect to the chemical potential. So this partial derivative, partial of Eu with respect to chemical potential of constituent i, while I keep fixed temperature, pressure, and the chemical potentials of all other constituents is equal to the negative of the amount of constituent i in the mixture.

So this thing here is minus ni. Then if I look in the previous slide and I look at the partial of mu with respect to T at constant p and n, that's minus s. That's the negative of the partial entropy. So minus and minus cancel becomes a plus. And so I have the summation of ni times si, whereas the first derivative here is here. It's minus S, capital S. It's the entropy of the mixture.

So if I now take this expression and rewrite it here, it says that the entropy of-- the overall entropy of my mixture is equal to the weighted sum of the partial entropies weighted by the amounts with which the constituents are present in the mixture minus a correcting term that has to do with the Euler free energy.

But if we are not interested in small systems, the Euler free energy is 0. And so in that limit, only the first term remains. And so we obtain that if I have these Si's, with them, I can compute the properties of my mixture. So I know the entropy of my mixture. And here, you can play the same game also for the volume. We skip this. We can play the same game also with respect-- when I do the partial derivative of Euler with respect to the amounts of one of the constituents.

If you do carefully the derivatives, as we are doing here, this becomes equal to this summation, which is written here again. And since, in the large limit Euler is equal to 0 identically, it means that this summation is equal to 0 identically.

Actually, there is one for each constituent because, you see, there is a summation over the constituents i. So i is a dummy index within the summation. But then there is a j, which is free. So this has to be equal to 0 for every j. This is called a Duhem-Margules relation. And it will play some role in making sure that when you develop models, you're doing it consistently. For the moment, we leave it there.

Now, in the next slide, I'm going to start from these three. So these three lines become the first lines here because, from these relations, I can prove similar relations also for all the other properties that we have talked about-- energy, Helmholtz free energy, Gibbs free energy, enthalpy.

So that means we can for all these-- and also, I can go it can go on to f, g, h, I have relations like that. If I want them for the mixture, all I need to do is play some derivatives of the chemical potentials. And with the proper relation, I get to the relation for the property of the mixture.

Of course, I need to also know the amounts. So I need to know the chemical potentials, how they depend on temperature, pressure, and amounts, and I need to know how many I have in my mixture. Yeah, I think time is up. So we could stop here.