

[SQUEAKING]

[RUSTLING]

[CLICKING]

**GIAN PAOLO
BERETTA:**

OK. Good morning. It will take us a couple of lectures, I guess, to cover this in some details. And it is-- we want to extend what we know about heat transfer to heat and mass transfer and charge transfer. And we want to do it in a way that exhibits the logic of the construction.

So this is why I am going to restart-- I mean, start again from what we have already seen because it already contains that logic. Actually, parallel logic between what we've done in chemical kinetics and what we've done in our simple review of the heat transfer basics. And because this contains what we want to develop item by item with some care and in other details in the rest of this lecture or two.

So in chemical kinetics, let's start with-- because we did this first, so let's start with this first. When we considered the closed systems, we considered the energy balance. It was implicit that the energy remains constant if the system is isolated. And this is the entropy balance that says that the rate of entropy change is equal to the entropy produced by irreversibility.

Then we-- this is not a balance of particles, but you could view the proportionality relations as sort of a balance in the sense that they account for the rate of change of the number of particles in your mixture. And so that is another ingredient.

Plus, we have assumed something about equilibrium-- the near-equilibrium situation in which we-- if it weren't for the chemical reactions that are changing the composition, our system in our model, so far, is very close to what it would be if it were in equilibrium-- a stable equilibrium state without the reactions on.

And that allows us-- so this relation here allows us to evaluate the rate of change of the entropy which is needed for the entropy balance. So we've to evaluate that. And when we do that rate of change, since this depends-- the only thing that is changing here is n through the proportionality relation-- so you have to take the partial of S with respect to n times the rate of change of n . And then you keep going and you single out the affinities of the reaction, and you bring in the reaction rates.

So you combine them, this balance equation, with the energy balance, which is trivial in this case, and you obtain an expression for the entropy produced by irreversibility, which is this product of rates and affinities that we interpreted as degrees of disequilibrium. And then we assumed a law that relates how the rates-- relates the rates to the affinities. And this law is a nonlinear law, but in the near-equilibrium limit, we have linearized it.

And here's the parallel structure and parallel logic that we followed when we derived-- when we did the heat transfer basis. We write the energy balance. It takes this form. We will return to why it takes this form. For the moment, just believe it. So that's the energy balance. This is the entropy balance. Also, of course, we will return on this. There is-- we are talking about a solid, a pure solid, there is no change in composition, so the rate of change of composition is 0.

Then we assume, like we did here, we assume something about the local equilibrium. We assume local equilibrium. So that there is a fundamental relation, we can write the Gibbs relation between the properties. And this is a way to write the Gibbs relation in order to-- we will also see this in more detail later. This is-- in order to get rid of the pressure here and push the pressure in the Gibbs-Duhem independent equation.

The Gibbs relation can be used to combine the left-hand sides of the balance equations. So you substitute the various balance equations into this Gibbs relation. And obtain an expression, like here, for the entropy produced by irreversibility. Of course, we will do the details. Also, because here, I've changed the notation a bit, but as you know, for a heat transfer, the energy flux is just q double prime, and the entropy flux is q double prime over T . That's the heat interaction.

And when we do these substitutions, you can rewrite the divergence of J_S as the sum of two terms. The first one cancels with the one that comes from the divergence of the energy flux. And you are left with this final result that says that the entropy produced by irreversibility-- and here, we are talking about entropy produced per unit volume-- is equal to the heat flux times the gradient in the inverse temperature, which we can interpret as the degree of disequilibrium for the heat transfer.

And then if we assume a linear law, then we get Fourier. In other words, if you-- by looking at this expression here, if-- and knowing that the entropy produced by irreversibility must be non-negative, the simple way is to assume that q is-- that the flux is proportional to the gradient through a positive constant of proportionality, which could end-- actually, since it is a vector, the most general linear relation between two vectors is through a tensor. So we take a positive tensor in between here, which assures that the sigma is going to be non-negative.

And then-- so we get Fourier law. And also, we have seen that if we accept Onsager's reciprocity theorem, that tensor not only needs to be positive definite-- or non-negative definite, but it also needs to be symmetric. You can also invert it. And therefore, the entropy production becomes a quadratic form in the degrees of disequilibrium, or equivalently, a quadratic form in the fluxes. OK.

So the ingredients are write the energy balance, do something about the Gibbs relation-- or write the Gibbs relation in this form so that you can combine these balances in a proper way. Make an assumption about the kind of interaction that is occurring between the various parcels or elements of your continuum. And then assume-- if you want to be near equilibrium, you can assume a linear relation.

And if you want to discuss more non-equilibrium-- I mean, not near-equilibrium-- far from equilibrium, then you need to develop some more elaborate theories.

And also, here, there is space, as we have seen for the Cattaneo correction to Fourier law, there is space to account-- or to solve some of the problems of the Fourier law, the infinite speed of propagation that is implied by this expression. So let's start. We take them one by one.

So we have to be patient, but this will give us also some opportunity to highlight a few of the details. This procedure that I am describing varies depending on the field of application. In particular, I need to mention, but I'm not going to follow precisely or-- but there is strong connections with a famous procedure called-- under the names of Coleman and Noll, which is used more by the community of solid mechanics people that study plasticity, viscoelasticity.

For example, not to go too far, if you go to Professor Lallit Anand in this department, he has written books and he is renowned for that procedure. I am more inclined, since I have studied with people in the fluid mechanics area, I am more inclined to describe the procedure that applies for fluid mechanics kind of applications. But the logics are very similar.

Except when it comes to this generalization of the heat interaction, that, instead, is peculiar, of course, of our course here because also, the definition of heat is peculiar to our course. Not yet very widespread in textbooks or other scientific papers.

OK, so let's start with this simple. Take a piece of material, fluid element. So already, the fact that I call it fluid means it shows you my inclination. And as you know, this department has had very influential professors in fluid mechanics. And heat transfer. So Rosenow, Shapiro, Sonin, just to mention a few.

So I have these one-dimensional piece of fluid. And it's subjected to interactions on one side and on the other side. And when we did heat transfer, we were considering only energy and entropy. Now here, we're going to introduce also a flux of particles. And also, here, you have the flux. And this is a component-- the x-component because we are one-dimensional-- of the flux, and it changes as you move from the face at x and the face at x plus dx .

And the area of exchange between the adjacent-- between these fluid element and the one to its right is A . And also, the area on the other side, of course, is, again, A .

We want to make a general energy balance, so we're not going to assume steady state. So we call the energy of the fluid in this lamina δE . Why delta? Because it's infinitesimal. Since the thickness is infinitesimal, it's from x to x plus dx . So that is an infinitesimal amount of energy. Related to the fact that it has an infinitesimal amount of volume, which is given by the area times dx .

And the specific energy per unit volume, you can write it, as we know, like ρ times u , and u here is really u^* , what we call the energy per unit mass. All right. So you write it-- you need volume, and then we can also substitute the volume for A times dx .

The same-- I mean, this system has also entropy. And here's the entropy. Also infinitesimal because it's an infinitesimal amount of material. And it stays like that. So it's the volume times the specific entropy per unit volume, which is ρ times s^* . And also the amounts, they are infinitesimal. And the amount per unit volume is the concentration. So you can write that as concentration times the volume. OK.

Now inside these element, we have also some volume effects. For example, chemical reactions that are occurring inside-- in the interior. And therefore, the proportionality relations are governed by this ϵ dot, which are the rates of advancement of the reaction coordinates. We can write also that as the volume times the reaction rate per unit volume, which is typically called r without the dot.

And then the other is the entropy production due to irreversibility, which occurs throughout the volume of this system. And that, too, we like to write in terms of per-unit volume. So we have defined this symbol s dot rate of entropy production. Triple means per unit volume, and soon, we have already started calling this thing σ . All right.

So here is the energy balance. It says the rate of change of the energy of our system is equal to the net energy it exchanges through the interactions. And here, it has interactions on the left and on the right. And the net is the difference. And you have to take it with a minus sign if it goes out. So if this one is greater than that one, the difference is this term here. And that is per unit area. And then you have to multiply by the area. And that is it, because energy is conserved.

Let's go to entropy. The entropy balance says the rate of change of the entropy of our fluid element is equal to the net entropy flux, via interaction. So here, I have, again, left and right. The difference is this term here. And with the negative sign because if it is positive, you have more entropy going out than coming in, and that's this term here.

I think there is an error here because I need also an area. Like here. I need to multiply by A . I need to correct that. That doesn't finish the entropy balance because you also have to account for the entropy generation inside the element due to irreversibility. Now what do we do? We simply divide by the volume ΔV left and right of these equations, and here is what you get.

So these are the balance equations. Now I want to open a little digression that is nevertheless important regarding how we describe the properties of a continuum-- in particular, the extensive properties like energy, mass, entropy, and a bunch of others that I'll have in a summary table.

So let's consider, like we typically do in fluid mechanics, we consider a volume. Call it σ_M . So it's a material volume. So I select at a certain instant of time a certain bunch of particles contained inside this volume. And I denote the surface of that as partial of σ_M . M stands for material.

Of course, when the fluid moves, you need to-- if you want to follow the material volume in all this problem, is that you need to track all the particles that are inside here at time, say, t_1 . And then at time t_2 , you need to see where all those particles have gone and consider another volume that contains only those particles.

And so these would be a Lagrangian point of view, and it's complicated, so that's why in fluid mechanics, you introduce control volumes and the Eulerian point of view. But that's not-- we're not doing control volumes here. They do them in fluid mechanics.

But what I'm doing here is just the balance equations, and in particular, I want to obtain from the balance equation written for the material volume, the balance equation written for the infinitesimal element of that volume. So in other words, something-- what we usually call the indefinite balance equations that are what holds point by point in our continuum.

So first of all, let's call the generic property-- think of energy, but then it could be also entropy, let's call it A , capital A . Or even mass. Even volume. And we call it extensive if you can say-- if you can assign to that property a local field little a . And field means it's defined at every point in space. x is x , y , z , and t is time. So this is the field. Like density.

So you want to-- you are assuming that you can define a density field as a function of position and time. So that you can write the overall property for the material volume as the sum of contributions for all the parts. So in other words, the integral of that property per unit volume times the volume. OK, so ρ times a is property A per unit volume.

OK. Once you have that, you have seen in the balance equations-- for example, the left-hand side of the energy balance or the entropy balance, you need to take the rate of change of the energy of your system or of the entropy of your system. So we need to take the rate of change, d by dt , of this integral to compute the left-hand side of the balance equations.

And since the material volume moves, you cannot just take the derivative inside the integral. Yes, you can, that does part of the contribution. But there is another part which is due to the fact that the limits of integration, namely this surface that follows the particles as they move, moves.

And therefore, you have to write a surface integral-- so an integral over the surface-- of-- that takes into account-- for each of these surface positions, you have to take into account-- first of all, you assign a unit vector. And by convention, usually I typically choose positive outward.

And then I have to see how the molecules on this point of the surface move. And that I call the velocity, v sub m . Which we will call soon the barycentric velocity. Because, in fact, before I call it v sub m , it simply should be the velocity assigned to the surface of the material volume. And then it turns out that since the volume is a material volume, so it's made of particles, that part of the surface moves with the velocity of the particles that are there. And the velocity of the particles is v_m .

So the net-- so since the velocity may have a different direction than the normal to the surface, what brings the particles, say, out of this volume and contribute to that surface integral-- or contribute to changing the surface integral is only the component that is in the direction of the normal. So that's why you take the scalar product of v and n to get the normal component that contributes to moving stuff out of that-- say energy out of that surface.

And then you convert by using the divergence theorem, a surface integral of this form something, dotted into n , is equal to the integral of the volume-- the volume integral of the divergence of whatever is dotted into n . And so you get this.

So we transformed this, the rate of change in an integral-- in a volume integral of two contributions, the partial with respect to t and the divergence of ρv_m . These will be called the convective flux in a moment.

Because that property that is exchanged-- OK. OK, we are talking about property A . So property A , like, say, heat-- I mean energy, if you have a heat interaction happening on the surface of this control volume-- so you have, say, another vector here, which would be q double prime, that is important in your energy balance because even if it is true that the surface follows the particles-- so the particles don't go out.

But if there is a heat interaction between those particles inside your material volume and those outside, then there is energy transfer between the two, and the energy transfer is represented by this vector here. And there is also, of course, an entropy transfer in the same direction if it is a heat interaction.

So what we define as flux-- because these are fluxes. So it's energy per unit area per unit time. Energy exchanged per unit area per unit time. And we give that-- the generic symbol J sub A -- or actually, J_0 sub A . And it's defined this way. And once I have defined that, I can also assign a velocity of transfer of that quantity. So I have the flux, to which is assigned the velocity of transfer, by dividing the flux by the property per unit volume.

So if I take q'' and divide it by ρu -- q'' divided by ρu , that gives me a velocity. We could call that velocity the transport-- the heat transport velocity. And also, you could have q'' over T , which is the entropy divided by ρS , and that would be the transport velocity for entropy.

The transport velocity for momentum (I meant, mass) is the barycentric velocity, the velocity that you typically use in fluid mechanics. If you say, the fluid has a velocity field v , you mean this velocity is the mass transport velocity. So it's J_m , which is the flux of mass, divided by ρ , because ρ is the mass per unit volume, and that is the barycentric velocity of fluid mechanics.

OK. Now-- so this velocity-- this flux with the 0 on top is, in terms of a reference frame-- yeah. OK. Reference frame the laboratory reference frame with respect to which you measure velocity of your fluid elements. However, you could also consider a local reference frame to your fluid element that moves with the velocity v_m .

So you move with your fluid element. Well actually, the fluid element is made up of many particles. So you have-- you're not moving with the velocity of one particular particle, but with a weighted average of the velocity, which is the barycentric velocity of those particles.

So relative to that, if I take the velocity of transport of this property, and I view it from that reference frame-- so the relative velocity is v_A minus v_m . So I define these flux. And we call it diffusive flux. So it's the flux relative to the local barycentric velocity.

This is the most practically used and what appears typically in the balance equations, but also, this other one appears. So you have to be careful if you are in this business and you see balance equations, you have to be careful whether-- because sometimes people don't put the naught. Actually, almost never put the distinction. They just pick one way of describing fluxes and then keep going, and presume that from the context of the paper, you can understand which one-- which is what.

Now the same concept of flux applies also, as you know, to vectors. So you can transfer momentum. And so if you define the diffusive flux where the property A is momentum-- actually-- so little a is the barycentric velocity itself. Then you obtain the diffusion-- momentum diffusion flux, which is the negative of the stress tensor. Also called the pressure tensor.

And typically, the stress tensor is split into two parts, an isotropic part with-- δ is like a tensor isotropic. So 1, 1, 1 on the diagonal and 0 off the diagonal. And that-- this is the trace of-- p_m is the trace of the stress tensor-- I'm sorry, of the pressure tensor, and divided by 3, and it is called the mechanical energy (I meant, mechanical pressure), which is not necessarily equal to the thermodynamic pressure.

OK. So what we instead call convective flux is the flux of that property which is transported by the simple translation of the fluid element. The fact that the fluid element moves, it brings with itself the properties that it has inside. So that produces a flux movement of the property. If there is energy in that box and you move the box, you're moving energy. So that is convection.

And it's the difference between this and the diffusive. Or, if you want, you can write the flux with respect to the reference frame as a sum of the diffusive plus the convective flux. OK. So the convective momentum flux is the fact that this fluid element, since it's moving, it has momentum.

And the momentum per unit volume is ρv . And since it's moving with velocity v , you're transporting momentum by simple motion. So it's not diffusion, it's just due to the fact that the thing is moving, and that is convective momentum transport.

Now inside your material volume, inside that fluid element, there are certain things that happen. For example, per unit volume-- for example, the entropy produced by irreversibility is locally produced. So it's something that when you want to account for it, you have to take it, multiply it by the volume, and then integrate.

So this you can view it as a source term. I mean, for the entropy balance, it's a source term. It cannot be a sink because it would violate the principle of entropy non-decrease. But in other models, for example, often in heat transfer, you use terms like-- you add a term to the balance equation, you call it triple prime q . It's the entropy-- I'm sorry, the energy-- internal energy deposited locally, for example, by joule effect.

If you have a conductor-- electricity conductor, by joule effect, that dissipates electrical energy and transforms it into internal energy. So if you make a balance of internal energy, you will find a source term, and that source term is a source-per-unit volume, so it's like a sigma of energy.

And usually you can distinguish between those that are produced by local effects-- like the joule effect is a local effect. Or a collision-produced effects, including chemical reactions, that essentially, chemical reactions, you can consider it as a source of products of the reaction and the sink for the reactants of the reaction, which occurs locally in your volume.

And so these-- you would call it with a superscript i . To be distinguished with the externally generated-- for example, if this fluid element lives in a gravitational field g . And, of course, it has mass. So it also has a potential energy. And the fact that it moves makes that potential energy change.

And that's not due to a local effect. It's due to an externally applied field. The same, if you had charges there and you had an electric field, say, an electric field like this. And then you move the charges-- so the electrical-- the electrostatic energy of your fluid element changes, and that gets into this volume term. It could be up or down, so it could be a sink or a source. So these in principle for various properties, could be positive or negative. It's only for the entropy production that you know precisely which sign it must have.

So finally, with all those ingredients, you can write the balance equations for this extensive property A . And it says the rate of change of the property inside your material volume is equal to the amount of-- the amount of-- the contribution of these sink source terms integrated, of course, over the volume. Minus the amount that leaves the volume through the surface.

And so that amount that leaves is equal to the velocity associated with the flux of that property relative to the velocity of the surface of your material volume. OK. Times the property per unit volume.

And also here, you see something dotted into n and integrated over a surface, you can use the divergence theorem and transform it into the divergence of whatever is dotted into the outward normal to the surface. And you may recognize here that since this velocity is v_m -- v_A minus $v_m \cdot n$ times ρa is the diffusive flux we defined it in the previous slide. That's why I get that.

So this is, the right-hand side of the balance equation. And the left-hand side we already wrote in a couple of slides ago. We wrote it in this form. So this is the general form of a balance equation for property A. For an extensive property A. And I think I'll repeat it in the next slide because we need to-- here it is. OK.

Now, since that equation-- balance equation must hold for whatever material volume, large, small, and so on, arbitrary, the only way that this equation can hold for arbitrary volumes is that the arguments of the integrals be equal, and therefore, you can cross away the integrals and keep the equality between the integrands, and that's your indefinite balance equation for property A.

Remember that we said that the diffusive flux is the Lagrangian flux minus the convective flux of that property. So we can combine these two equations, and therefore, rewrite it in either this form or that form. These are two equivalent ways to write the balance equation.

But the important thing is that in this left-hand side, you get J_0 , whereas here, you get J . And these combination of partial derivative and the barycentric velocity times the gradient of property A, which comes in when you substitute these into there, as you know, it's called the material derivative.

And it represents how things change as a function of time as viewed from the fluid element by moving together with the fluid element at the barycentric velocity. And following, therefore, the fluid element. That's why it follows the trajectory that is called the path line in fluid mechanics.

OK. So these are the balance equations. We are going to-- I think we are going to use-- well, either one. Probably more this one. So if you do that, what we have done for the one-dimensional problem, if you do it for the three-dimensional-- I mean for the full-dimensional stuff, you can write the mass balance equation in this way. You can write the energy balance in this way in terms of the diffusive fluxes. The entropy balance.

But also, you can write the momentum balance. And, of course, the material-- actually, these two are related to one another. Because what you would need to do is to write a balance equation for each kind of particle, each type-- like each i . And then once you have it, you can express it in terms of mole-specific or mass-specific and so on.

And you can write it-- for example, here, this symbol ξ is the mass fraction. In other places-- actually, probably in the next slide, I call that same mass fraction with the symbol x .

So here is the definition of the barycentric velocity that I mentioned, and here is the expression for the flux of-- the mass flux in laboratory frame. It's ρ times v . And it is related to the mass and to the velocities of the various (constituents) and this table, I'm not describing it, but simply is there.

It's useful just to mention how many different ways you have to do the accounting, and depending on what your application or depending on your community, people use mole fractions, mass fractions, concentrations, and so on. And so these are the interrelations that intercur between these various properties. So I'll leave it there just for reference.

And also, this slide provides a list of examples-- the main examples for those extensive properties that we have written the balance equations for. And for which we can define convective fluxes and diffusive fluxes.

And so the number of moles, the total mole, the mass of particles of a certain type, the total mass, the charge of particles of a certain type, the total charge, the energy, the entropy, the kinetic energy, the potential gravitational energy, the potential electrical energy, and momentum. For each one of these, you can write balance equations of the form-- of the generic form that we have discussed.

OK. So that is the balance equation. Now, just a small digression about the fact that we are dealing, in this model so far, and all that we have done, we are dealing with the idea of a continuum. The fact that you can assign to a position in space and time a-- for example, a density, it means that you have enough particles in your volume so that you can-- so that you can assume that all the particles are-- so that you can take the mass of the particles and consider it as uniformly spread in that volume.

And that you can do only-- of course, that is a limit of the traditional fluid mechanics. And you can do it only if the Knudsen number-- the Knudsen number is the ratio between the mean-free path-- mean-free path is the travel distance that, on average, particles travel between one collision and the next. So that is λ .

And in the denominator is L . L is the typical size of your fluid mechanics-- it's the length scale of your fluid mechanics problem. Could be the boundary layer thickness or could be the diameter of your pipe if you are in a pipe flow. So not always the Knudsen number is smaller than 1. Smaller than-- much smaller than 1.

So typically, one would say, if it is less than 1%, then you can apply the continuum hypothesis. If it is not, then you have to be careful because the results that you are obtaining may not correspond to the physical reality. So you can always do that in the model, but the results are not providing valid descriptions of reality.

For example, this table gives for air. At sea level for dry air at 25 C, 1 atmosphere. The mean-free path, it's about 67 nanometers. So this condition is guaranteed when you see the green. So if I have a device that is a large, small-- even pretty small, like 70 microns, it's pretty small, you still can apply fluid mechanics.

When your device gets smaller-- see, the denominator of the Knudsen number gets smaller, so the Knudsen number becomes larger. And so for small devices, you cannot-- we cannot use fluid mechanics or the continuum assumption. But even for air, if you go at this position, 100 kilometers altitude-- it's called the Karman line, there, the temperature is minus 80 degrees C and the pressure is hundreds of atmospheres.

The mean-free path is about-- what is it? 100 times-- 50 times larger than at sea level. So there, it's the λ that is high.

So even for standard devices-- for example, a typical problem where the Knudsen number fails and you cannot apply fluid mechanics, it's in the boundary layer of the space vehicles that have to come back to the atmosphere, in the upper layers of the atmosphere, the λ is so small (I meant, large) that the Knudsen number is of the order, say, 1 even for relatively large thicknesses.

And therefore, that was, in fact, one of the problems when they were studying the reentry problem of the Space Shuttle. And not only-- also the-- the other vehicles that have re-enter through the atmosphere.

OK. So remember that what we are doing refers to a continuum, so there are limitations to this. At the end, one of the final lectures we'll mention what we need to do when this fails.

OK. Now we are in the part that we have to-- in order to assemble the energy balance, entropy balance, constituents' balance, we need to use a Gibbs relation to combine them, which is an assumption of local equilibrium, which goes together with the continuum assumption.

So remember, you have the Gibbs relation. We are talking about large number of particles, so we assume the Euler relation, and also from the two, we get the Gibbs-Duhem relation. Now here, there are a couple of-- OK, so that is the basics. Then, of course, we need to remember what the definitions are, chemical potentials. We've seen it so many times. The differential of the chemical potential, if you remember when we started doing mixtures, we wrote this expression here.

A new way that is used often is this one. You collect the part of the differential that is not related to changes in temperature. And instead of writing it all the times explicitly, you write it as the differential-- the part of the differential of μ that would survive if you keep the temperature constant with this symbol here.

So you change the chemical potential by changing the temperature. And so the specific-- I'm sorry, the partial entropy appears here. And you call the rest, which relates to changing pressure and composition, you put it together in here.

Then, another item that we do because we are making balances, for example, of energy-- not of internal energy. Yes, we could also make a balance of internal energy, but usually, the meaningful one is the energy balance.

And so in the energy balance, we typically use this bulk flow-like expression of the energy in which we recognize an internal energy, and then some mechanical addenda that bring in the kinetic energy, the gravitational potential energy, the electrostatic potential energy, and even the centrifugal potential energy with the negative sign that we have seen when we did the stratification.

And you remember that, therefore, the chemical potential gets in-- it's only a part of the expression of the partial of the energy with respect to the amounts, which we have called the total potential.

And there are these other contributions that need to be taken care of. There is some-- there is some fishy-- this dq -- this dq shouldn't be here. Yeah, it's from cut and paste from this expression where I take this one, I take the differential here, and then you take the total potential is the partial of the energy.

While you keep fixed the entropy, the volume, the other amounts, and then you have to keep fixed, for example, the barycentric velocity, the height in the potential, the value of the gravitational-- I'm sorry, of the electrostatic field, the angular speed, and the location. So you keep all these fixed and change only the amount of that particular constituent in order to get the total potential.

And these last lines are just a summary of the fact that you can write properties-- specific properties per mole, per unit mass with the star, or per unit volume. Per unit volume, you could write it as ρu star, or also c times u . So this is a summary of what's needed.

So we have worked so far using molar specific properties. And the Gibbs-Duhem relation has been always written this way. And with this new notation of the differential of the chemical potential at fixed temperature, it takes this form. And since that differential means any changes of the property-- if you change only the property by moving in space at a given instant of time, that becomes-- you can substitute, essentially, the d with the nabla, with the gradient.

And so you have an expression here that comes from the Gibbs-Duhem and gives you the gradient in pressure and how it is related to the gradients in the chemical potentials. So they are not independent. It's just another face of the Gibbs phase rule. You may also write it in terms of mass-specific properties. I'm not staying too much on this. You can just-- but I'm staying more on this other one, volume-specific properties.

Because if I write the Gibbs relation, the Euler relation, and the Gibbs-Duhem relation in terms of these volume-specific properties, what I already said is that you can show that the pressure disappears from the Gibbs relation. Not that you get rid of it, but in terms of these volume-specific properties, you decouple the Gibbs relation from the Gibbs-Duhem relation.

And you can so forget about pressure, and then when you need it, you can use the Gibbs-Duhem relation as an additional independent equation that gives you the pressure. So the gradient in pressure is the weighted sum of the gradients in the chemical potentials, the constant temperature part, weighted on the concentrations of the various things.

So this Gibbs relation, you can write it-- this time, we are interested in the change with respect to the time variable while keeping the position variables of these fields constant. So you may substitute the d with the partial with respect to t . So that Gibbs relation becomes this one. Or gives this relation between the partial properties (I meant, partial derivatives).

And as you notice, these are the left-hand sides of the balance equations. This is the left-hand side of the energy balance, left-hand side of the entropy balance, left-hand side of the constituent's balance.

Now we need to generalize the idea of heat interaction. And we do it in a way similar to the way we have done the heat interaction. So simply here, it's drawn in a different way. Remember, we took two systems that are at different temperature, and we allow them to exchange energy and entropy, and then we run a test. Can we identify part of that energy that is transferred between the two as work? If yes, we don't call it heat. If no, yes, that's the condition for a heat interaction.

So in order to analyze this problem, you run an energy balance and entropy balance for system A. Same for system B. Same for the machinery here. We use the Gibbs relation for system A. We use the Gibbs relation for system B. And outcomes that the work-- the maximum work-- so we set the entropy generation equal to 0-- the maximum work you can get is given by the Carot coefficient multiplied by the energy that is being transferred.

And so that says that, yes, a good fraction of that energy can be recognized as work unless the Carnot coefficient is equal to 0. And that is why we define heat only when the two temperatures, T_A and T_B , are-- their difference vanishes, so they are approaching each other.

And also, in addition to this result, you remember that we get a set of inequalities that says that the entropy exchanged is bound, has an upper bound and a lower bound related to the initial temperatures of the two objects, and only in the limit in which the two temperatures are equal to one another, that range of values results in a single definite relation between the entropy transfer and the energy transfer. Which is this relation-- q , or δq , because then we call that heat, is equal to T times the entropy exchanged.

Now if we divide by the area of contact between the two objects-- so A here represents the area, not the system A , and dt is the amount of time that the interaction occurred, you obtain the flux. So you may rewrite this expression as saying that for a heat interaction, the energy flux and the entropy flux are related by the temperature, which is this, this expression here. And actually, for this particular one, we could even write q double prime, the symbol q double prime for heat. OK.

Now I do the same, but with a new fact that the two systems, the two-- think of them as the adjacent fluid elements that for which we are making a balance. But in general, these two systems exchange not only energy and entropy, but also a given amount of each of the constituents.

The procedure is the same. You have to write energy and entropy balances for system A , for system B , and for the machinery here. And you need to use the Gibbs relation for system A and the Gibbs relation for system B . It's a bit improper how I'm doing it here because the pressure-- there should be a pressure term there if we are not using properties per unit volume. But anyway, the idea is still OK.

And then as a result of these balance equations, you get this expression. So the question is always the same. Can we recognize as part of the energy that is being exchanged here, part is work? Well now, we have two ways in which we could. If the Carnot coefficient is different than 0, then a good fraction, yes, could be work. But also, if these other coefficients-- I don't know what the name is, but if it is different than 0, then even if the temperatures are equal, you could have some work.

So in order to have-- to extend the idea of heat interaction-- and we are going to call this new interaction heat and diffusion interaction with the ampersand that joins them-- for lack of better names, we call it heat and diffusion, you need the limit that the temperatures be equal, but also the chemical potentials of each of the constituents of the two interacting systems be equal.

And of course, by the same way that we prove that inequality, you could prove this inequality here, that the entropy exchanged is, again, limited by two-- an upper bound and a lower bound, which, in that limit, become the same value, and in that limit-- so for a heat and diffusion interaction, you have a definite relation between the energy that is transferred, the entropy that is transferred, and the amounts of constituents that are transferred.

And if you divide by dt and the area, the various transfers, you get the fluxes. So it's the transfer per unit area per unit time. And so this is the relation that characterizes-- it's the equivalent of q over T , but you see here that it contains also this part. So this is a very important new independent equation that we need in order to-- like we needed the q over T in order to combine the energy and entropy balances. Here it is. So we start from that.

The question now is-- I see something fishy with this slide, but in any case, the question is-- I'm sorry. The question is, can we still call heat the energy that is transferred in a heat and diffusion interaction? The answer is no. Only part of the energy transfer can be called heat.

How do we identify that? OK, remember-- OK, we start from this relation between the fluxes that characterizes the heat and diffusion interaction. The chemical potential appears in it. Remember that the chemical potential can always be written as the partial enthalpy minus T times the partial entropy for each of the constituents. This is general.

So substitute that. And then take, on the left-hand side, the stuff that is not multiplied by T , and on the right-hand side, the stuff that is multiplied by T . So now you have found some part of the energy transfer of the energy flux-- the total minus this part-- which is related to a part of the entropy flux, via the temperature. So we are going to call that part of the energy flux q double prime. That is what we call the heat flux.

So we call heat, only the difference between this and the flux of constituents, each multiplied by the partial enthalpy. You can think of this term that we are subtracting away as the energy that is carried by the particles that diffuse because J_n is the diffusion (flux) of particles of type i .

These particles diffuse, and therefore, carry with them-- like in their backpack, they have the partial enthalpy and the partial enthalpy-- they actually have the partial energy and the partial entropy. But in order to overcome-- to move in a pressure field, they have to-- that's why get the enthalpy and not the energy, it's like in bulk flow, you have the pulsion work.

This is pulsion work against the partial pressure, but it's still something that takes you from the energy plus the work that is needed to overcome this-- the pulsion work. The partial pulsion work.

So the overall energy flux is, therefore, now given by this that we will call heat, plus this transported enthalpy due to the flux of particles. And also, the entropy flux is given by q over T . So that's proper of a heat-- characteristic of the heat interaction. Plus the entropy that is carried in the backpack by these particles that are diffused. So in other words, by calling this q double prime, essentially we are transforming this single equation into two equations with the q double prime in it. And so we have these two sets.

In heat transfer, we call it q double prime. In this typical business of non-equilibrium thermodynamics, this is called the measurable heat flux, particularly introduced by this famous bible of the subject, which is the book by De Groot and Mazur.

If the particles carry also charge, then we do exactly the same. So the relation that defines the heat and diffusion interaction is like this, except that you have to substitute the chemical potential with the total potential, so it becomes this one. And remember that the total potential when you have particles is given by this. It's the chemical potential, plus the electrostatic potential times the charge of-- the unit charge of your particles. So you can write it this way. Still in terms of the chemical potential.

So now you can still use the fact that the chemical potential is h_i minus Ts_i . And then you can also-- remember that-- or define. If you take the flux of particles-- and these particles carry this much charge. This flux of charge is what we call current density-- charge current or electrical charge current density.

So take this one or this one and substitute as before and-- not substitute-- and move left-hand side the stuff that is not multiplied by T and on the right-hand side the stuff that is multiplied by T , then you recognize-- then you call-- define q double prime, the measurable heat flux, as this term here, and you get two equations.

So now, the energy flux is due to heat. The energy transported by the diffusion of particles through the enthalpy, the internal energy plus the pulsion work, and the electrical energy carried by the charge carriers. And for the entropy flux, the same. There is no contribution by the electric charge current.

So with these ingredients-- Yeah we're almost out of time, but yeah, we can-- well, yeah, one-- let me just say-- one thing from which we will start next time is that you can rewrite that expression that defines the relation between energy, entropy, and materials flux in an entropy form instead of an energy form in terms of new variables, like the inverse of the temperature and the chemical potential, the total potential divided by the temperature. But let's do that next time because we're out of time now.